REPORT NO. HDC-51-79

ANALYSIS OF WASTEWATER FOR ORGANIC COMPOUNDS UNIQUE TO RDX/HMX MANUFACTURING AND PROCESSING

FINAL ENGINEERING REPORT

B. R. Stidham

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HOLSTON DEFENSE CORPORATION
Subsidiary of Eastman Kodak Company

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Sensitive analytical methods were developed for the direct determination of RDX, HMX, TAX, SEX and TNT in wastewater. Reverse Phase HPLC and direct injection of the aqueous sample extended the statistical lower detection limit for each component to less than 65 µg/l. RDX, HMX, TAX and SEX were the only nitramines detected in wastewater at the Holston Army Ammunition Plant, and only RDX and HMX were detected in Holston River water one mile below the last plant effluent. Four cyclohexanone-derived compounds were identified as probably constituents of plant wastes; one, or possibly two, of these were found in the Holston River.

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Analysis of Wastewaters for Organic Compounds Unique to RDX/HMX Manufacturing and Processing

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INTRODUCTION

This project was undertaken to identify and quantify munitions-unique compounds in wastewaters associated with the manufacture of RDX, HMX, and special formulations of these two high explosives at Holston Army Ammunition Plant (HSAAP). Such compounds could potentially reach the environment. Data so obtained would assist the U. S. Army Medical Bioengineering Research and Development Laboratory to assess the environmental hazard of these compounds.

The overall project was divided into two phases having the following specific objectives:

Phase I - Identify the waste stream organic pollutants unique to RDX/HMX manufacturing and processing.

Phase II - (a) Standardize analytical methods for determining organic components in RDX/HMX waste streams.
(b) Determine the decomposition rates (hydrolysis) of the potentially toxic compounds and verification of their persistence in receiving waters.

The objectives of Phase II were modified through the course of the project so that the final phase consisted of:

(a) Isolation of concentrates for identification of constituents by an independent laboratory under contract to USAMBRDL.

(b) Development and evaluation of analytical methods for chemicals identified and monitoring of effluents and receiving waters (Holston River) over an extended period.

The major emphasis of Phase I was to identify the constituents of the RDX and HMX process wastewater contributing the largest wasteload to the industrial sewer. These streams were less diluted with cooling water than the outfalls; thus, the constituents were at higher concentrations than would otherwise be available. Subsequent work in Phase II made use of the concentrated stream to provide isolates for identification and used the dilute outfalls and the river for final methods development and monitoring of identified constituents.

BACKGROUND

General

A meeting was held at Holston Army Ammunition Plant (HSAAP) on January 28, 1974 with representatives from the U. S. Army Armament Command (ARRCOM), Holston Army Ammunition Plant (HSAAP), Holston Defense Corporation (HDC), and Environmental Quality Division of USAMBRDL (U. S. Army Medical Bioengineering Research and Development Laboratory) to: (1) advise all concerned agencies of the need for special toxicological work to provide a data base for materials unique to munition plants; (2) express the urgent need for expedient responses in the initiation, processing, and implementation of funding and contractual mechanisms for procuring required support; and (3) solicit Holston's assistance in performing chemical studies on HSAAP wastes, an essential prerequisite to initiation of the toxicological studies.[1]

A need was indicated for special chemical studies to define the potentially toxic components of the wastes unique to RDX/HMX manufacture and stated that the chemical study was on the critical path of the overall project and that delays in the characterization of waste streams would result in similar delays in the toxicology work.

The assistance of Holston Defense Corporation in performing the work was pursued in great detail. The uniqueness of the wastes and Holston's capability for providing the analytical expertise and technology supported the opinion of the Surgeon Generals Office representatives that Holston was best qualified to conduct the chemical studies.

Holston Army Ammunition Plant (HSAAP)

Holston AAP is a government-owned contractor-operated (GOCO) installation under the jurisdiction of the U. S. Army Armament Command. The Holston Defense Corporation, a subsidiary of Eastman Kodak Company, is the operating contractor of the plant. The mission of HSAAP includes the manufacture of high explosives and chemical material as assigned and to handle and store for other government agencies, strategic and critical materials as directed. RDX and HMX and formulations (using chemical additives or TNT) are the only high explosives manufactured at the plant. HSAAP is the only facility in the DOD available for and engaged in the manufacture of nitramine based high explosives.

HSAAP consists of two plant areas, Area A and Area B, on the Holston River. The two plants are connected by a land corridor (approximately 6 miles in length) on which is located connecting chemical pipelines and intra-plant railroad.

The operations at Area A provide for the manufacture of acetic anhydride and the concentration of weak acetic acid, recovered at Area B, to yield

glacial acetic acid. The operation at Area B consists of explosives manufacturing, nitric acid manufacturing, and recovery of weak acetic acid. This report concerns only the explosive manufacturing at Area B, because of the uniqueness of the operation.

The explosive manufacturing consists of 10 RDX/HMX production lines for full mobilization. During this work only two lines, one each RDX and HMX were in operation. A flow diagram of the RDX/HMX manufacture process including its relationship to the nitric acid, organic acids (Area A), and acetic acid recovery (Primary Distillation) are shown in Figure A-1.* A schematic of a "line" facility is given in Figure A-2.

The primary source of nitramine pollutants in wastewater is the dewatering process at the H-Building, and limited amounts of dewatering at a G-Building. A second source of nitramine and TNT pollutants occurs as the result of decanting water from molten castables (Composition B, Cyclotols, Octols, and Composition B-4) at the incorporation buildings. Presently, the industrial wastewaters exit the buildings to an interceptor sewer system which releases the materials to the river without benefit of treatment. The construction of a central wastewater treatment facility to serve both Area A and Area B has begun. All industrial wastewater will be processed through the plant, which is expected to be operable by late 1982.

* All figures and tables for the main body of this report are given in Appendix A.

CONCLUSIONS

1. Sensitive analytical methods were developed for the direct determination of RDX, HMX, TAX, SEX and TNT in wastewater. Reverse Phase HPLC and direct injection of the aqueous sample extended the statistical lower detection limit for each component to less than 65 µg/l.

2. RDX, HMX, TAX, and SEX were the only nitramines detected in wastewater at HSAAP. TNT was also detected in the wastewaters. The component concentration ranges were as follows in the effluents over six weeks of monitoring.

	mg/l
RDX	0.110 to 16.02
HMX	0.090 to 3.36
TAX	5.24 maximum
SEX	2.03 maximum
TNT	2.01 maximum

3. RDX and HMX were the only nitramines detected in river water approximately one mile below the last plant effluent. The concentrations of 79 and 67 µg/l were much higher than should have been obtained based on mass quantities and river flow. This is attributable to incomplete mixing of effluents in the river.

4. Four compounds, unrelated to nitramines or nitroaromatics, were identified in cyclohexanone wastes that may originate during recrystallization of RDX. The compounds are:

   2 hydroxymethylcyclohexanone

   spiro-1-oxocyclohexane-2,2', 3', 4', 5', 6', 7', 8' -hexahydro-benzo-b-pyran

   2-(2-cyclohexenyl) cyclohexanone

   2-(1-cyclohexenyl) cyclohexanone

   Components having equivalent retention times by gas chromatography were detected in the effluent and Holston River. However, the consistency of concentrations in all samples suggests that the responses were not unique to nitramine manufacturing operations as they probably are formed when cyclohexanone is heated and may be present as impurities in purchased solvent.

EXPERIMENTAL AND DISCUSSION

EXPERIMENTAL[1] - Phase I

Sample Collection

A review of active production buildings was performed and the following points chosen as representative of RDX and HMX manufacturing buildings contributing pollutants to HSAAP Waste Streams: (a) outfalls from production lines 6 and 7 (one outfall designated Lines 6-7), (b) outfalls from production lines 1 through 5 (one outfall designated Lines 1-5) and (c) catch basins at the following production buildings: E-6, E-7, G-3, G-6, H-6, and H-8. (Figure A-2, schematic of Typical Production Line. The alphabetical character prefix refers to the building type and the numerical suffix designates the line in which the building is located.)

Grab samples were obtained and stored in polyethylene bottles until they could be concentrated. No special storage conditions were employed. Preliminary results of chromatography screening of concentrates showed very few components from these points prompting further review of potential sampling points. Considering the large dilution factor caused by process cooling water in the main outfalls, various process contributions of pollutants, and sample concentration time requirements, it was expedient to sample the "dewatering" (of RDX and HMX slurries) process streams which are the major sources of nitramine pollutants in HSAAP's waste streams. Samples of the "dewater" filtrate were taken from the overflow of the settling tanks at Building G-6 (HMX) and Building H-7 (RDX) for final concentration and subsequent fractionation.

Sampling points are shown in Figure A-3.

Sample Concentration

Carbon Adsorption

It is widely known that activated carbon will absorb organic compounds quite efficiently from water, particularly when such compounds are present in low concentrations and are only slightly soluble. A feasibility test was performed to provide an indication of the applicability of this technique to removing organic compounds from the RDX and HMX waste water samples selected for treatment.

Activated carbon (Pittsburgh Activated Carbon, Type CAL, Grade 12 x 40) in a 0.61 m x 50.8 mm (3 ft. x 2 in.) glass column was used in attempts to adsorb selected organic compounds (acetic acid and cyclohexanone) from aqueous solution. Total carbon analyses of the starting material and the liquid after it had been passed through the column showed 80% of the added organic compounds were adsorbed on the activated carbon. However, neither solvent washing nor Soxhlet extraction techniques proved to be effective in recovering the organic compounds from the type of activated carbon available at the time this experiment was performed.

Liquid-Liquid Extraction

Liquid-liquid (countercurrent) extraction, another widely used sample concentration technique was investigated for applicability to RDX and HMX wastewaters. Several solvents with densities greater than and less than that of water were considered,as solubilities of RDX and HMX in various solvents were reviewed.

Solubility data showed that RDX and HMX are only slightly soluble in solvents that are immiscible with water.[3] Consequently, continuous liquid-liquid extraction did not appear to be an ideal method. The technique was evaluated, nonetheless, because of potential capability for rapid treatment of large volumes of water.

A specially designed liquid-liquid extraction apparatus was used to extract organic compounds from wastewater. Ethyl ether was used as the extraction medium. Two extractors were used to extract 8 liters of wastewater simultaneously. The following wastewater samples were extracted.

(1) Lines 6-7 Outfall, 12 liters extracted
(2) Lines 1-5 Outfall, 12 liters extracted
(3) Catch Basin Water from Production Buildings E-6 (HMX), E-7 (RDX), G-3 (RDX), G-6 (HMX), H-6 (HMX), H-8 (RDX) and filtered water, (8-20 liters of each extracted).

Freeze Drying

The inadequacy of the liquid-liquid extraction method for extracting solids in sufficient quantities led to efforts to freeze-dry waste water samples. Excessive time was involved in freeze-drying of water samples; therefore, only two sampling points, RDX dewater and HMX dewater streams, were chosen since they would contain the highest concentrations of pollutants unique to RDX/HMX manufacturing. Samples were taken of the overflow from the "dewater" settling tanks for concentration by freeze-drying.

The freeze-drying apparatus, Virtis Model Nos. 10-131 and 10-117-A, consisted of the following: vacuum pump, freeze drying chamber (8 port), condensate trap, and freeze-drying flasks. The coolant used to freeze samples and to trap water consisted of a dry ice and acetone mixture. Approximately one liter of dewater yielded approximately 200 mg (0.2 grams) of freeze-dried solids. These solids were submitted to E. I. DuPont Analytical and Physical Measurements Services (subcontractor) for identification analyses (Appendix B).[4]

Evaporation

A steam-heated, rotary vacuum evaporator was also used to concentrate water samples because it provided more rapid removal of water than did freeze drying. A comparison between freeze dried and evaporator-prepared solids by liquid chromatography methods showed that significant thermal degradation of components had not occurred in the steam-heated system. This conclusion was arrived at by comparing chromatograms relative to numbers of, and intensity of the component peaks.

Analytical Separation and Identification

Gas Chromatography

The ether extracts from the liquid-liquid extraction method were analyzed by gas chromatography using a Perkin Elmer Model 900 gas chromatograph. Isothermal operations, helium carrier gas, and a flame ionization detector were used. The columns used for chromatographing the samples are listed below:

(1) 10% UC-W-98 on Chrom G-AW-DMCS 0.61 m x 6.3 mm (2 ft. x ¼ in.) glass column
(2) 10% UC-W-98 on Porapak Q-S 0.91 m x 3.2 mm (3 ft. x 1/8 in.) stainless steel column
(3) Porapak R 1.83 m x 3.2 mm (6 ft. x 1/8 in.) stainless steel column
(4) 1% Carbowax on Graphitized Carbon - 0.91 m x 3.2 mm (3 ft. x 1/8 in.) stainless steel column.

All of the above columns were used in attempts to chromatograph the ether extracts. Failures to obtain any GC responses indicated no volatile components were extracted.

Liquid Chromatography (LC) and Infrared Analyses (IR)

The ether extracts were also analyzed by liquid chromatography using a Waters Associates Model 202 Liquid Chromatograph equipped with an ultraviolet (UV) detector. A stainless steel column 0.15 m x 3.2 mm (6 in. x 1/8 in.) packed with Micro Partisil^{R} using a solvent system of 15% acetonitrile, 15% methylene chloride, and 70% hexane, was employed.

Solids recovered by vacuum evaporation of the water at 20°C were tested in HDC Laboratories. Analyses (See Figures A-5 and A-6) consisted of fractionation using a Waters Associates liquid chromatograph equipped with a UV detector and a gradient elution attachment. A stainless steel column, 0.15 m x 3.2 mm (6 in. x 1/8 in.) packed with Micro Partisil was used. A mobile phase solvent system of methanol, acetonitrile, and chloroform with hexane as the gradient solvent, was employed. RDX dewater (Bldg. H-7) solids were fractionated (Figure A-4) into 13 major fractions and the solvent evaporated at room temperature. HMX dewater (Building H-7) solids were fractionated (Figure A-5) into 9 fractions. Infrared analyses were performed on the RDX dewater fractions (as time allowed) before submissions to the subcontractor, DuPont (Table A-1).

Infrared analyses were performed using either KBr discs or an oil mull and a Beckman Model IR-10 infrared spectrometer.

Subcontract Work

The freeze dried solids were not tested at HDC. These solids and filtered water extract were shipped to E. I. DuPont Analytical and Physical Measurements Service for identification analyses. Also, a data package consisting of infrared and NMR scans of available reference compounds and twelve reference standard samples (Table A-2) were shipped to DuPont to aid in analytical work. The report (DuPont Report No. 754-81) is attached (Appendix B).[4] Only RDX, HMX, TAX and SEX were identified in the fractions sent to DuPont (Table A-3). Their work indicated possible presence of a compound containing acetyl and N-NO_2 functions, with a cyclic backbone in the RDX dewater. This unidentified component probably was TAX as the compound may also exist in the RDX process.

EXPERIMENTAL AND DISCUSSION

EXPERIMENTAL[5] - Phase II

Collection of Samples

As determined in Phase I, the major sources of nitramine pollutants in HSAAP wastestreams were the filtrates ("dewater") from the aqueous RDX and HMX slurries produced in the respective recrystallization processes. Dilution of the filtrate was minimized by collection of samples of "dewater" from the overflow of the settling tanks at Building G-6 (HMX) and Building H-3 (RDX) RDX dewater (68.4 l) and HMX dewater (67.5 l) were obtained from these buildings for final concentration and subsequent fractionation.

Sample Concentration

Work in Phase I showed several methods of sample concentration to be inadequate for nitramine compounds in RDX and HMX dewaters. A method employing a microreticular resin (XAD-2 manufactured by Rohm and Haas) as the adsorption medium was adapted to use on wastewaters. The resin was washed with methanol and placed in a glass column, 0.92 m x 7.6 cm (3 ft. x 3 in.) with glass wool plugs on the bottom and top of the resin column. The column was filled with sample and allowed to flow by gravity through the resin. The organic components were desorbed from the resin by washing with a methylene chloride/acetonitrile (88:12 v/v) solution. Organic compounds were recovered by evaporation of the solvent at room temperature in a laboratory hood. This method showed a 85% recovery efficiency using known concentrations of nitramines. The RDX dewater solids were obtained by passing 68.4 l of dewater through 350 g of XAD-2 resin with subsequent desorption with 4 l of methylene chloride/acetonitrile (88:12, v/v). Solids (22.5 g) were recovered by evaporation of the solvent at room temperature. These were dissolved in acetonitrile for fractionation by HPLC. HMX dewater solids (13.9 g) were obtained from dewater samples in the same manner.

Analytical Separation and Identification RDX and HMX Dewater Solids

Fractionation of the acetonitrile extracts of RDX dewater solids was performed using a HPLC preparative method. A Waters Associates Model 202 Liquid Chromatograph equipped with an ultraviolet (UV) detector set at 280 nm and provisions for gradient elution was employed. A stainless steel column 30.5 cm x 12.7 mm (12 in. x 0.5 in.) packed with 5 micron (mean particle size) LiChrosorb Si60 was used with a solvent system of hexane (weak solvent) and acetonitrile/chloroform (2:3 (v/v) strong solvent) in the gradient (solvent delivery) mode. A solvent flow rate of 7.0 ml/min was used with 1.4 ml injection of the solution containing the

solids at a concentration of 46.7 mg/ml. Eight fractions from each of 40 injections were collected using an automatic fraction collector. The collected fractions were evaporated to dryness at room temperature in an exhaust hood. Two of the 8 fractions, were judged to be minor components based on the peak area percent (4.4) and weight (21 mg) of solids (2.5 g injected) obtained after evaporation of the solvent. Six of the isolated fractions (minimum 50 mg each) were prepared for shipment to Midwest Research Institute (MRI) for identification. Three of the 6 fractions were extracted with chloroform and/or carbon tetrachloride and analyzed by infrared spectroscopy prior to shipment to MRI.

Fractionation of HMX dewater solids was performed in the same manner as RDX dewater solids. Sixty one injections of a 24.1 mg/ml solution were made yielding 6 fractions, two of which were determined to be minor components (2.02% of total peak area). Therefore 4 HMX dewater solids fractions and 6 RDX dewater solids fractions were shipped to MRI for identification analyses. Total weight of each fraction was in excess of 50 mg.

Three of the six RDX dewater fractions were identified as RDX, TAX, and SEX by MRI. Three were judged to be too impure for identification. Two of these contained no $N-NO_2$ bonds and are probably cyclohexanone derivatives. Three of the four HMX dewater fractions were identified as RDX, HMX, and SEX. One was judged too impure for identification but contained no $N-NO_2$ bonds. Thus, the special analytical work by MRI identified only RDX, HMX, SEX, and TAX in effluents from MRI in agreement with the Phase I work.[6]

Cyclohexanone Wastes

The XAD-2 resin adsorption method was used for collection of compounds which are solids at ambient temperature. Cyclohexanone, the primary solvent used in recrystallization of RDX, was sampled after it had been recycled extensively in the process to facilitate identification of related volatile components present in HSAAP's wastewaters. The solvent was distilled to concentrate volatile and residual impurities. A portion of the first 10% (by volume) distilled and a portion of the 10% remaining in the still pot were sampled. A second distillation was performed, simulating the solvent clean-up procedure used at HSAAP. A portion of the non-volatile material which would normally be discharged into the wastestreams was retained. These three portions were shipped to MRI for identification analyses. Four cyclohexanone-related (see Analytical Method Development section) compounds were identified in the cyclohexanone wastewater samples by MRI.[7] These compounds were:

2-hydroxymethylcyclohexanone	I
spiro-1-oxocyclohexane-2,2', 3', 4', 5', 6', 7', 8' - hexahydro-benzo-b-pyran	II
2-(2-cyclohexenyl) cyclohexanone	III
2-(1-cyclohexenyl) cyclohexanone	IV

There was no confirming evidence that any of these compounds were present in the effluent wastewaters.

Reference Compounds and Data Package

The following data and reference compounds were provided to MRI to support their identification analyses (Appendix C).

(1) Sixteen reference (nitramine - related to RDX/HMX manufacturing process) compounds were shipped to MRI.
(2) HPLC chromatograms of these reference compounds along with relative retention times.
(3) HPLC chromatograms of the fractions using two separate HPLC columns (different from one used for fractionation), LiChrosorb Diol and Partisil PAC (cyano).
(4) HPLC chromatograms of RDX dewater solids and HMX dewater solids that were fractionated for shipment to MRI.
(5) Infrared spectra of some of the dewater fractions of the reference compounds.
(6) Gas chromatographic scans of the three cyclohexanone distillates.

Analytical Method Development

The second portion of Phase II consisted of monitoring HSAAP waste streams for the nitramine pollutants identified by MRI. Therefore an analytical method capable of measuring these nitramines (RDX, HMX, SEX, TAX) and TNT in milligram/liter and microgram/liter ranges was needed. Chemical nomenclature and trivial designation are given in Table A-3. Also, a method for measuring cyclohexanone-related compounds (identified by MRI) was needed. A description of the development of these methods follows.

HPLC for Nitramines and TNT

Concentration and HPLC

Previous HPLC work at HDC has shown that chromatographic separation of nitramine compounds can be greatly altered by column functionality and mobile phase composition. A silica column and three types of column functionalities were tried: diol; amino; and cyano. Silica gave the best separation of the several nitramines likely to be encountered during analysis.

As the columns with different functionalities were being investigated so were the following solvents (all UV grade): methanol; acetonitrile; tetrahydrofuran; dioxane; 2-ethoxyethanol; formaldehyde; chloroform; hexane; iso-octane; and distilled water. Reverse phase separations at this time were not as efficient as the absorption separations using the silica column with a mixed solvent as the mobile phase. The mobile phase giving the most efficient separation was 5:10:15:70 (v/v) methanol: acetonitrile: chloroform: iso-octane, in the isocratic mode. This mobile phase composition was arrived

at by varying the number and amounts of solvents until no components were eluted at t_0 (retention time of unretained components), baseline separation between components was achieved, and total analysis time was minimized. Sample injection volume was determined by performing multiple injections using sample loops (injector valve) of different volumes. Maximum injection volume was found to be 30 microliters as evidenced by peak shape and repetitive area counts (integrator). Table A-19 contains this data.

A Micromeritics HPLC equipped with a variable wavelength detector (Chromonitor Model 785) was employed for nitramines and TNT detection. The optimum wavelength for this particular detector was determined by analyzing the same solution from 235 nm to 280 nm in 5 or 10 nm increments (Table A-4 and Figure A-6). A check of the total percentage difference between 240 nm and 245 nm revealed 245 nm to be the best wavelength for TAX and SEX. Use of a lower setting would have increased sensitivity to TAX but caused a greater decrease in sensitivity to SEX. This specific detector does not allow accurate wavelength calibration, thus these maxima were at higher wavelength settings than the true maximum for nitramines.

Detection limits using the above HPLC columns, wavelength, mobile phase, and injection volume were determined. Detection limits for RDX and HMX were found to be approximately 5 mg/l (Table A-19)). This was not suitable because RDX and HMX concentration levels in some wastestreams and the Holston River were known to be in the microgram/liter range. Therefore a concentration method was necessary for application of HPLC in the microgram/liter range. Previous work in concentrating dewater solids showed XAD-2 resin to be efficient (85%) for absorbing organic compounds from water, with subsequent removal of the compounds with organic solvents. Adsorption was performed by gravity flow through the methanol washed resin in a 0.92 m x 7.6 cm (3 ft. x 3 in.) glass column. The organic compounds were extracted from the resin by using methylene chloride: acetonitrile (88:12, v/v). The solvent was removed by evaporation from open beaker at room temperature in an exhaust hood. The resultant solids were dissolved in acetonitrile for HPLC analyses. Final instrument parameters were as follows (Figure A-7).

Instrument:	Micromeritics Model 7000B
Detector:	Micromeritics Chromonitor Model 785 (variable wavelength UV)
Wavelength:	245 nm
Column:	Stainless steel, 30.5 cm x 6.4 mm (12 in. x 0.25 in.), packed with LiChrosorb Si60, 5 micron MPS
Mobile Phase:	5% methanol, 10% acetonitrile, 15% chloroform, 70% isooctane
Flow Rate:	2 ml/min
Injection Volume:	30 microliters
Recorder Chart Speed:	0.5 in/min
Integrator:	Spectra Physics System IV

Reverse Phase HPLC - Direct Injection

As the preceeding HPLC method was being evaluated, new technology was being developed on other projects at HDC that exhibited excellent possibilities for adaptation to wastewater analysis. A reverse phase HPLC system was developed that allowed for large volume-direct injection of water samples. Preliminary investigations showed that nitramines and TNT separation was good in the isocratic mode with detection limits in the low mg/l range. Conversion to the gradient elution mode gave indications of detection in microgram/liter range. This could be accomplished by loading of the front of the column with constituents from aqueous samples because the weak solvent (water) would not elute the components. Introduction of a strong solvent via gradient elution desorbed the constituents and further aided component separation.

Based on these preliminary results, the reverse phase - direct injection HPLC method was adopted. Refinement was made by switching from isocratic to gradient elution. This not only shortened components,elution time but allowed for larger injection volumes when using water as the weak solvent and methanol: acetonitrile as the strong solvent. A solvent program of 0-40% (weak-strong) in 5 minutes was used. Injection volumes from 30 microliters to 1.5 ml were tried with the optimum (detection versus component separation) injection volume of 0.7 ml being selected. Detection of less than 0.1 mg/l of nitramines and TNT was possible using this method. Therefore, the concentration method was eliminated because of superiority of the newly developed procedure. The new method reduced analysis time, and improved precision and accuracy by avoiding tedious analysis steps and minimizing potential degradation or sample loss. The evaluation of this method relative to this application follows on page 15.

Method refinement produced the following instrument parameters for the reverse phase-direct injection HPLC method (Figure A-8).

Instrument:	Micromeritics Model 7000B
Detector:	Micromeritics Chromonitor Model 785 (variable wavelength detector) at 230 nm.
Column:	Stainless steel, 30.5 cm x 6.4 mm (12 in. x 0.25 in.) packed with RP-8 LiChrosorb, 10 micron, MPS
Mobile Phase:	Weak - water; strong - methanol; acetonitrile (2:1, v/v)
Gradient Curvature:	Concave 1
Gradient Range:	0% weak to 40% strong
Gradient Time:	5 min.
Flow Rate:	3.0 ml/min.
Injection Volume:	0.7 ml
Recorder Chart Speed:	0.5 in./min.
Integrator:	Spectra Physics System IV

A deterioration of the source lamp for the variable wavelength detector occurred during refinement of the reverse phase HPLC method. Lamp replacement and calibration of wavelength were performed. The optimum wavelength for nitramines had changed from a setting of 245 nm to 230 nm for the UV detector. This new wavelength was obtained by determining reponses for an aqueous solution of nitramines (one mg/l) at wavelengths downward from 245 nm (no wavelength tried above this as sensitivity started increasing for the lower wavelengths).

Gas Chromatography (GC)

The following compounds related to cyclohexanone were identified by MRI from the cyclohexanone distillates:

2-hydroxymethylcyclohexanone	I
spiro 1-oxocyclohexane-2,2', 3', 4', 5', 6', 7', 8', hexahydrobenzo-b-pyran	II
2-(2-cyclohexenyl) cyclohexanone	III
2-(1-cyclohexenyl) cyclohexanone	IV

Compounds I, II, and III were supplied in 1 gram quantites by MRI with a purity of 99+%. The fourth (IV) compound was purchased by HDC. Attempts to chromatograph these compounds by HPLC was abandoned due to the large number of component peaks observed using two different HPLC methods. At this point gas chromatographic analysis was attempted using a Perkin Elmer Model 900 Gas Chromatograph. Isothermal operation, helium carrier gas, and a flame ionization detector were employed. The columns used are listed below:

(1) Chrom W + 3% OV-1, 1.85 m x 3.2 mm (6 ft. x 0.124 in.) stainless steel.
(2) Porapak P-S, 1.85 m x 3.2 mm (6 ft. x 0.125 in.) aluminum (teflon lined).
(3) Porapak S, 0.92 m x 3.2 mm (3 ft. x 0.125 in.) aluminum (teflon lined).

None of the four compounds were detected using column 1; all were eluted on 2, but the retention times were long (22 min.) and the component peaks were too wide for quantitation; all were eluted using column 3 with an analysis time of 8 minutes. Compounds I and II had the same retention time as did III and IV. Final GC instrument parameters are as follows: (Figures A-9 and A-10).

Instrument:	Perkin Elmer Model 900 Gas Chromatograph
Detector:	Flame Ionization
Column:	Porapak S, 0.92 m x 3.2 mm (3 ft. x 0.125 in.) aluminum (teflon lined)
Oven Temperature:	250°C
Manifold Temperature:	225°C
Injector Temperature:	225°C

Carrier Pressure:	52 psi
Carrier Flow:	60 ml/min
Hydrogen Pressure:	30 psi
Air Pressure:	52 psi
Attenuation:	X4
Recorder Chart Speed:	0.5 in/min

Analytical Method Evaluation

Concentration and HPLC

An extensive evaluation of the HPLC and XAD-2 resin concentration methods was undertaken. A plan for evaluating the analytical method was designed on the basis of the method of Hubaux and Vos so that a useful range of analysis and the accuracy of the method could be determined from one set of data.[8]

Standard solutions containing RDX, HMX, SEX, TAX, and TNT were prepared. The compounds were dissolved in a minimum quantity of acetone and subsequently diluted with distilled water to 4 l to give the concentrations shown in Table A-5. The standard solutions volumes of 4 liters were taken through the concentration (4 l to 50 ml) step prior to HPLC analysis (Figure A-6). Quantification was by use of Spectra Physics Model IV integrator. Reference samples (external standards) were analyzed at the same time as standard solutions for calculation purposes. HPLC results obtained by analyzing these standards are also in Table A-5. These standard solutions were in the milligram/liter range. Original plans called for evaluation of the method in microgram/liter range, but at this point, a switch to the reverse phase-direct injection method (Figure A-8) was made because of low overall recovery efficiency noted for several of the compounds.

Reverse Phase HPLC - Direct Injection

An extensive evaluation of the reverse phase-direct injection method was undertaken using the experimental plans formulated for the original HPLC and concentration method. Standard solutions (100 ml) of RDX, HMX, SEX, TAX, and TNT in distilled water were prepared by dilution of an acetone stock solution for analysis. Precision and accuracy were determined by performing multiple injections of mixtures of the standard solutions. Solutions containing the five components in concentrations of 1, 6 and 10 mg/l and 50 and 200 µg/l (Tables A-6 through A-10, respectively) were analyzed. The experimental plan for determining the lower detection limit called for preparation of solutions containing TNT and the nitramines, identified by MRI. Six standard solutions were prepared in the range of 0.5 to 16 milligrams/liter. HPLC analyses produced the results and subsequent statistical evaluation in Table A-11. Five standard solutions were prepared in the range of 10 to 200 micrograms/liter. HPLC analyses produced the results and statistical evaluation in Table A-12. The lower

detection limits for each of the compounds are also listed in Table A-12. The computer program supplied by Dr. E. W. Sarver (ARRADCOM Chemical Systems Laboratory) to evaluate the data on the basis of Hubaux and Vos technique was adapted to use on the G. E. time sharing computer at HDC.

Gas Chromatography

The GC method of analysis used to determine the cyclohexanone related compounds was evaluated as to lower detection limits by use of the Hubaux and Vos method. Solutions containing known quantities of the four components over the range of 5-100 mg/l were analyzed to establish the lower detection limits (Table A-13).

Wastestream Monitor

Sampling

A review of active production buildings and the wastestreams serving these buildings was performed. Three industrial effluent streams (underground sewers) were selected because they contained all the manufacturing and processing water produced at Area B (process cooling water not included in this). Two sampling points (Figure A-3, points 2 and 3) serving lines 6-7 and 1-5 and one sampling point (Figure A-3, point 4) serving part of line 1 and the acid area. The fourth sampling point (Figure A-3, point 4') was the receiving waters for these wastestreams, the Holston River. Sampling point 4' was at the boundary of HSAAP on the plant side of the river approximately one mile below the lower plant effluent. This point was selected with the hope of having the most representative sample after mixing of the wastestreams and river water.

Portable-automatic streams samplers (Manning Portable Samplers, Model S-3000 Composite) were used for collection of samples. The samplers were set at a rate of 200 ml per hour for a time period of 24 hours. An aliquot (500 ml) of each sample was saved for analysis. The pH of each sample (Table A-14) was checked and the solution was acidified with acetic acid if on the basic side. The pH was adjusted to preclude any possible degradation of the nitramines during refrigerated storage. A record of the production buildings operating during each sampling period was made (Table A-15). (Figure A-2 is a schematic showing the function of production buildings in a typical production line.) Flow rates of each wastestream and the Holston River were taken during the sampling period (Table A-16). The flow of the Holston River was obtained by converting river stage readings at the filter plant to flow rates.

HPLC Analysis

The monitor was initiated on May 10, 1979 with samples collected on May 11, 1979. HPLC analyses for nitramines and TNT were initiated at the end of each 24 hour sampling period and completed by the following day (Table A-14, Figures A-11 and A-12). One set (4) of samples per week for each of 6 weeks was

taken and analyzed. The first set of samples taken was analyzed 3 times over the duration of the monitor other than the initial analysis. This was done to determine if any degradation of the nitramines or TNT occurred during refrigerated storage (Table A-17). From one to five extraneous peaks were found in HPLC chromatograms of samples analyzed. The retention times of the extraneous components did not agree with known retention times of other nitramine reference compounds. Retention times of these components were in the area where low boiling solvents are known to elute using the HPLC reverse phase mode.

The total mass per day of RDX and HMX in the effluents was calculated on the basis of concentrations found and stream flows (Table A-16). The mean daily quantities of nitramines delivered to the river, based on the four 24-hour monitor periods, were 156 lbs (70.8 kg) RDX, 45 lbs (20.4 kg) HMX, 49 lbs (22.2 kg) TAX, and 33 lbs (15.0 kg) SEX. The low daily emission from the plant through the three effluents is in agreement with historical emission quantities. Therefore, the concentration in the river appears to be higher than theoretically possible based on effluent concentrations. This high bias is attributed to incomplete mixing of the effluent with the river at the sample point. The two high RDX concentrations detected for sample point No. 3 on May 10 and May 29 are attributed to known spills of RDX/wax resulting in an increase in the soluble fraction in the effluent.

Gas Chromatographic Analyses

Gas chromatographic analyses were performed on the monitor samples to determine concentrations of the 4 cyclohexanone related compounds (Table A-18). The concentrations shown for Compounds I or II could be either or a combined total of both, calculated as Compound I. Compounds III and IV were not detected in any samples and if present were below the lower detection limits as established in the method evaluation section. The consistency of concentrations of Compounds I and II in the effluents and Holston River could be due to interferences in the GC method of analysis.

References

1. R. A. Jackson, "Report of Meeting: Environmental Quality Standards Research-Water-Pollutants, "Holston Defense Corporation, Memorandum to Dr. Robert Robbins, January 31, 1974.

2. Fortson, H. D. and Stidham, B. R., Holston Defense Corporation Research and Development Notebook No. 100, pages 1 through 76.

3. Engineering Design Handbook - Properties of Explosives of Military Interest, Report No. AMCP 706-177, page 73, January 1971.

4. A. J. Dahl, "Separation and Analysis of RDX and HMX Dewater Solids", E. I. DuPont DeNemours & Company, Analytical and Physical Measurements Service, Report No. 754-81, 6-19-75.

5. Stidham, B. R., Holston Defense Corporation Research and Development Notebook No. 1084, pages 1-100 and Notebook No. 1132, pages 1-73.

6. Danny O. Helton, "Identification of Waste Products from RDX and HMX Manufacture", Midwest Research Institute Subtask 9, Monthly Report No. 15, November 9, 1977.

7. Danny O. Helton, "Identification of Waste Products from RDX and HMX Manufacture", Midwest Research Institute, Subtask 9, Monthly Report No. 17, July 27, 1978.

8. A. Hubaux and G. Vos, Analytical Chemistry, Volume 42, No. 8, pages 849-855, July 1970.

9. G. C. Bassler, "The Chemistry of Cyclonite", Thesis, Pennsylvania State College, October 1943.

10. Acheson J. Duncan, Quality Control and Industrial Statistics, Richard D. Irwin Inc., 1959.

11. W. J. Youden, Statistical Techniques for Collaborative Tests by the Association of Official Analytical Chemists Inc., 1967.

APPENDIX A

Tables and Figures

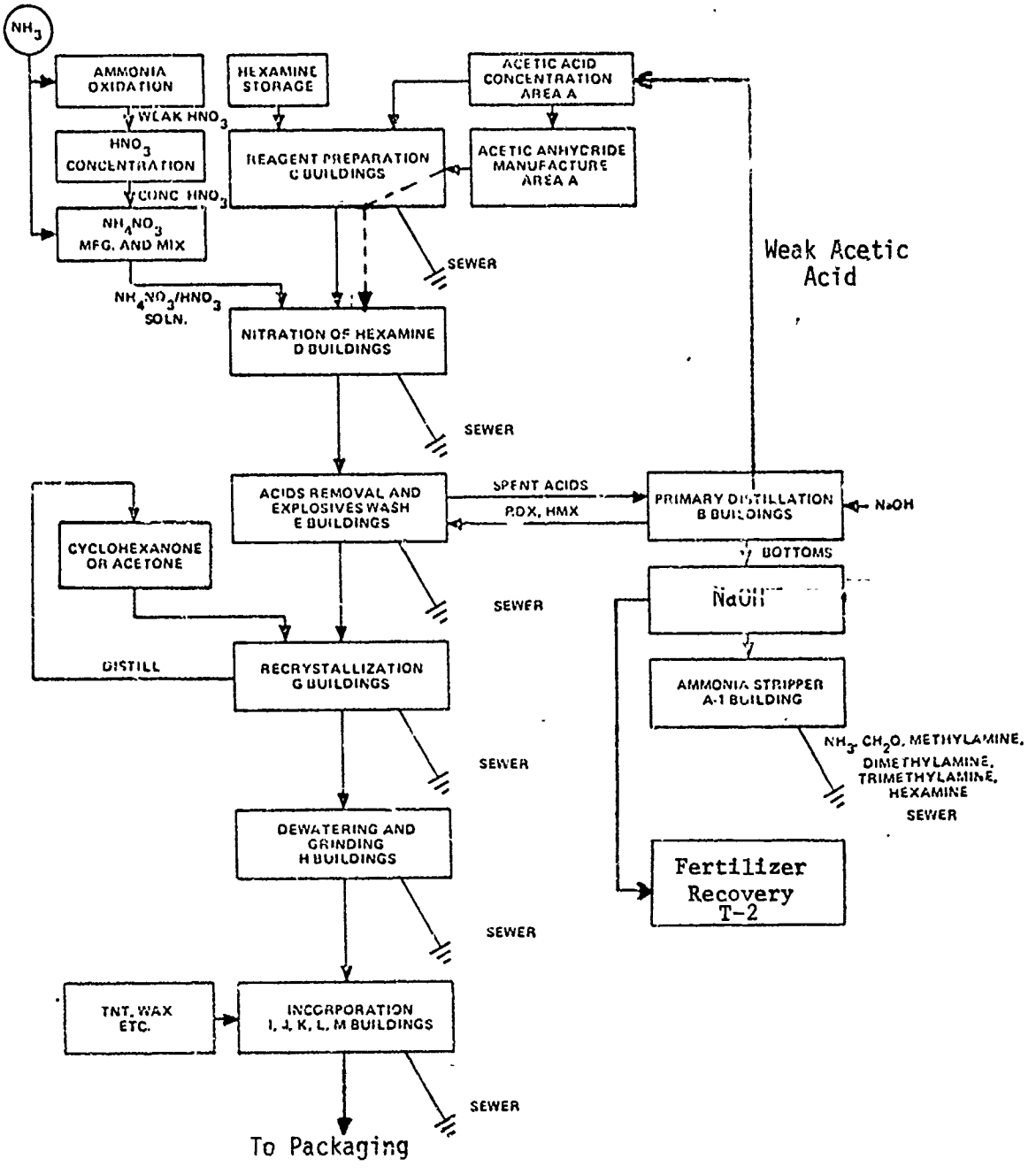


Figure A-1. Flow Diagram of the RDX/HMX Manufacture at Holston AAP.

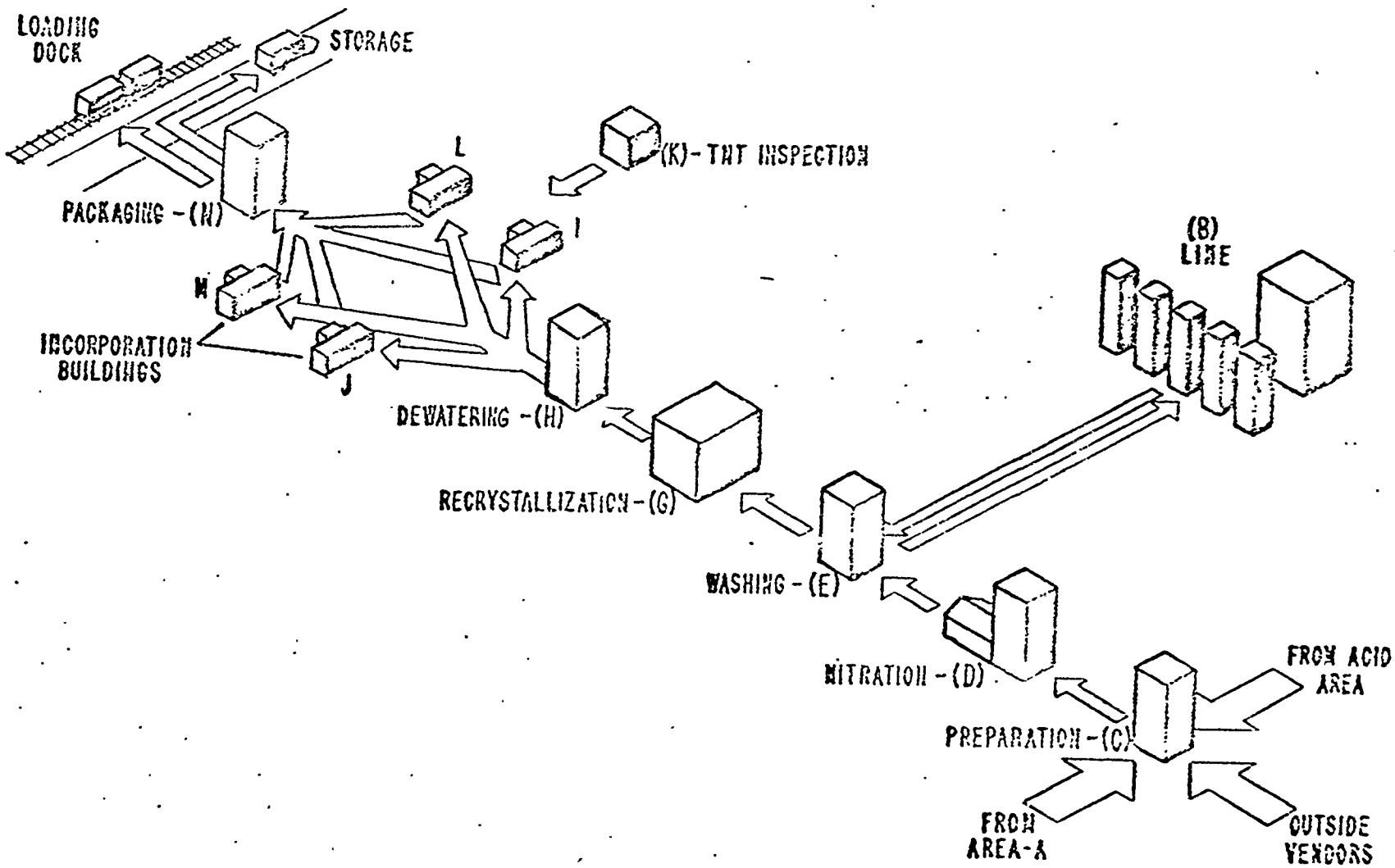


Figure A-2. Holston Army Ammunition Plant Schematic of Explosive Production Line Area B

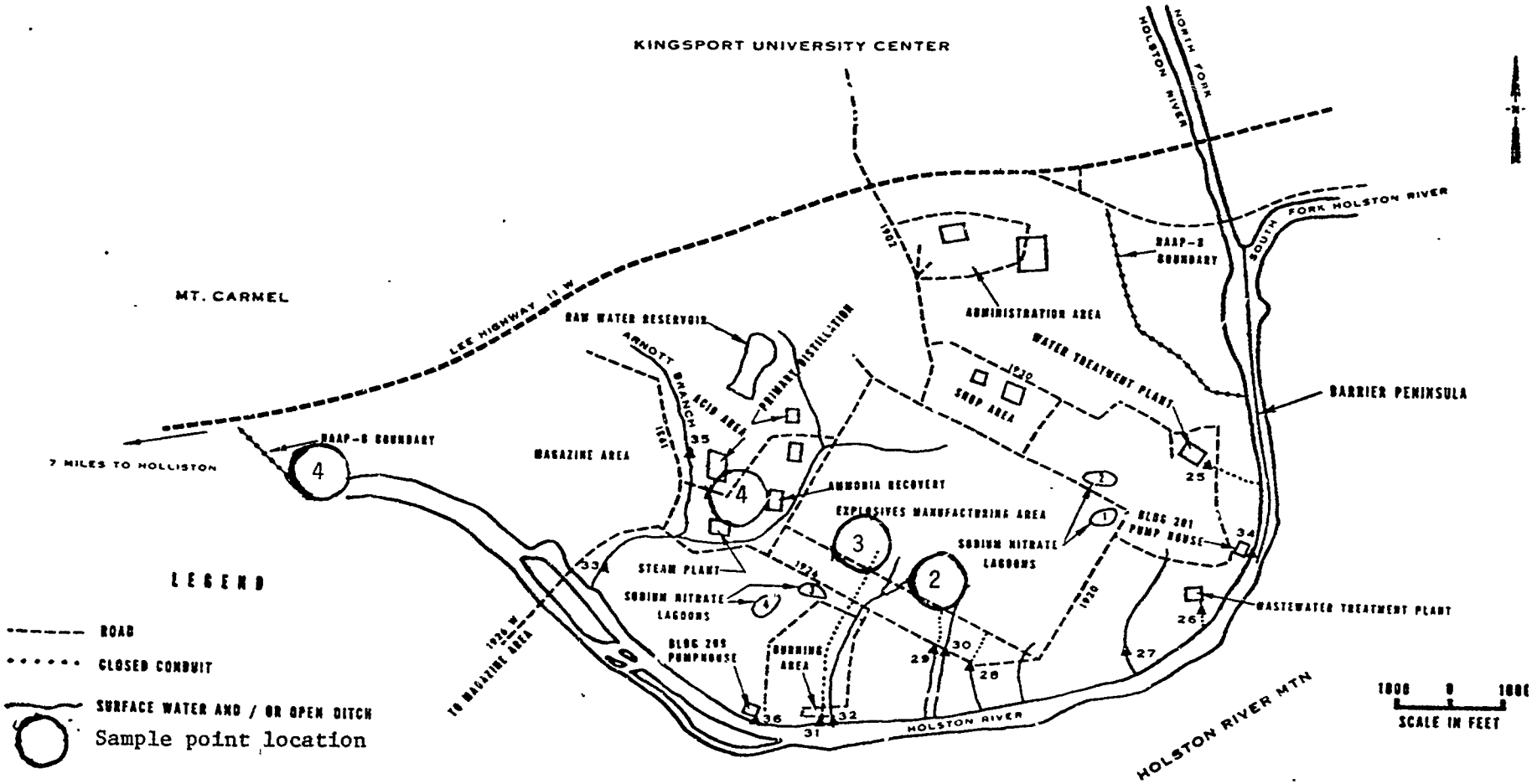
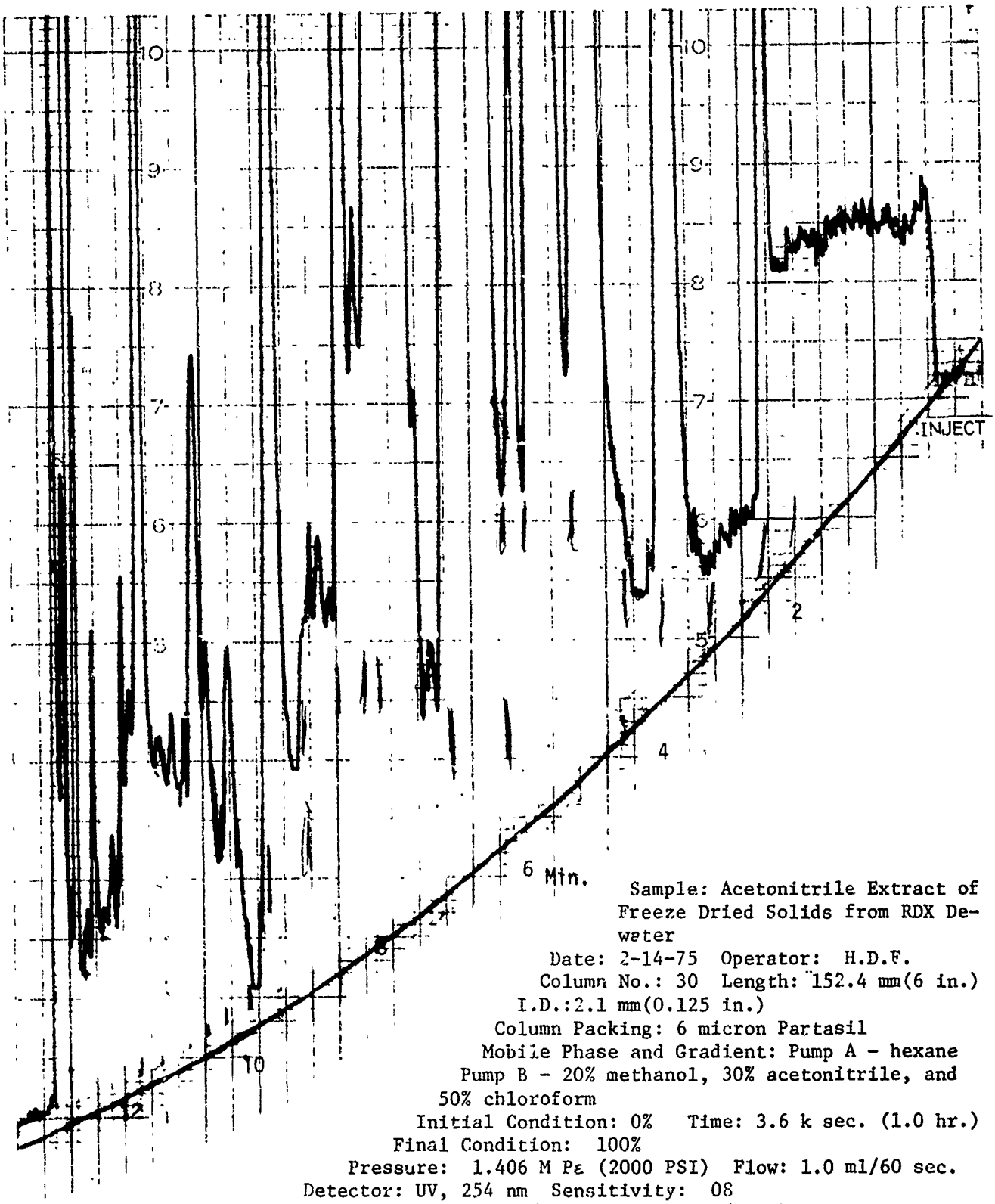
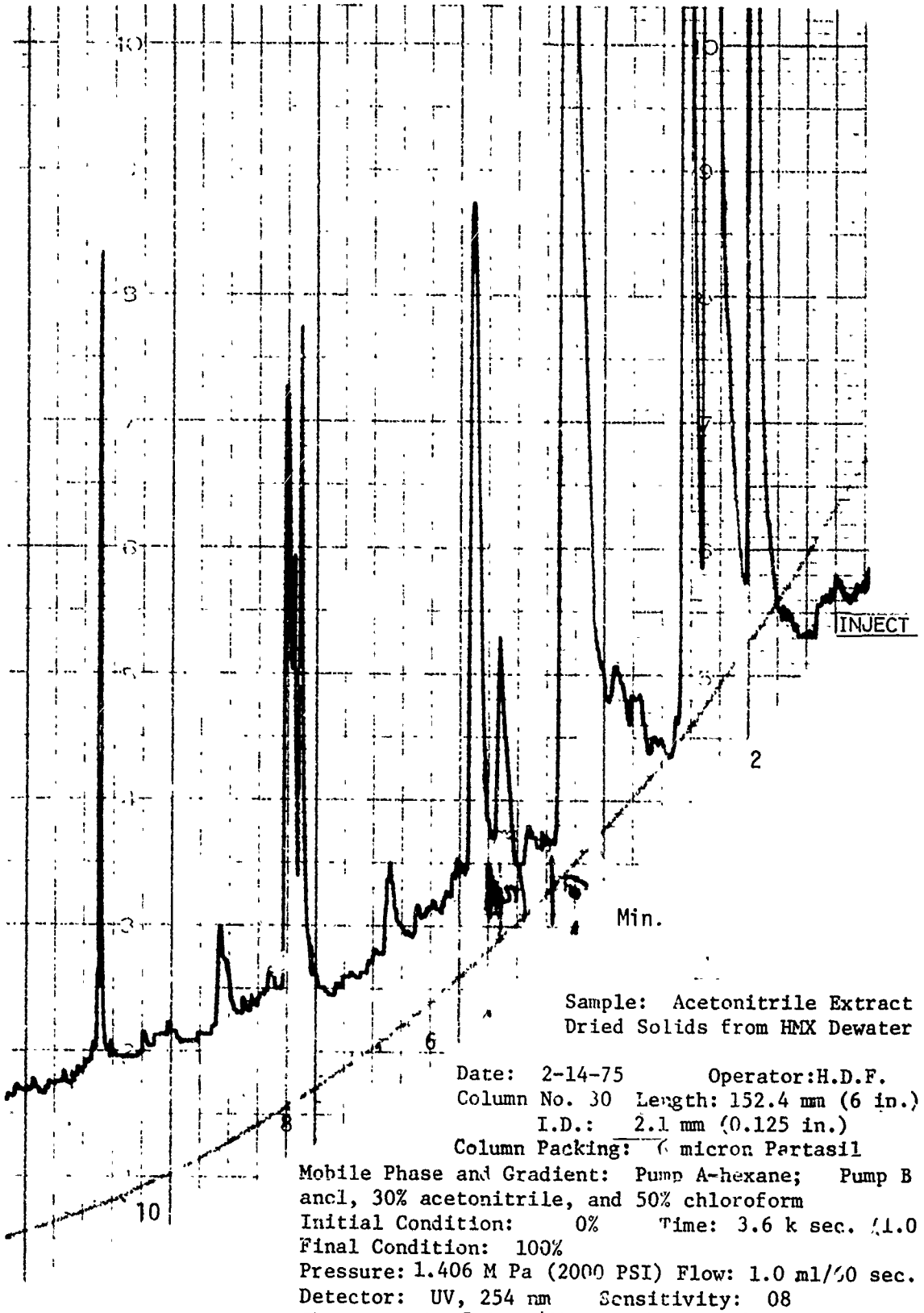


Figure A-3. Holston Army Ammunition Plant - General Location of Sampling Points



Sample: Acetonitrile Extract of Freeze Dried Solids from RDX Dewater
Date: 2-14-75 Operator: H.D.F.
Column No.: 30 Length: 152.4 mm(6 in.)
I.D.:2.1 mm(0.125 in.)
Column Packing: 6 micron Partasil
Mobile Phase and Gradient: Pump A - hexane
Pump B - 20% methanol, 30% acetonitrile, and 50% chloroform
Initial Condition: 0% Time: 3.6 k sec. (1.0 hr.)
Final Condition: 100%
Pressure: 1.406 M Pa (2000 PSI) Flow: 1.0 ml/60 sec.
Detector: UV, 254 nm Sensitivity: 08
Chart Speed: 5.1 mm/60 sec. (0.2 in./min.)
Gradient Curve: No. 7
Injection Amount: 10 microliters

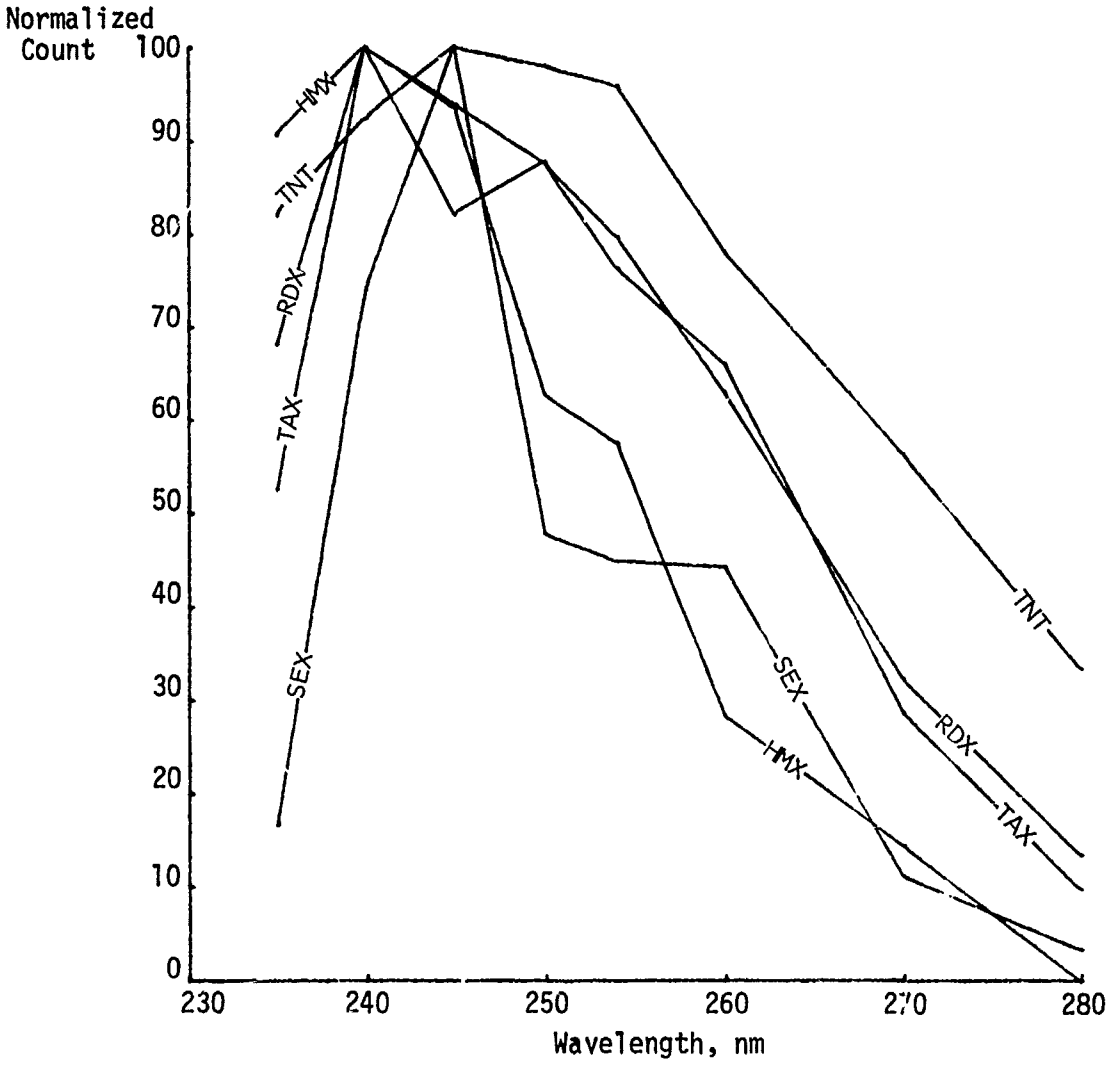
Figure A-4. HPLC Chromatogram of RDX Dewater Solids



Sample: Acetonitrile Extract of Freeze Dried Solids from HMX Dewater

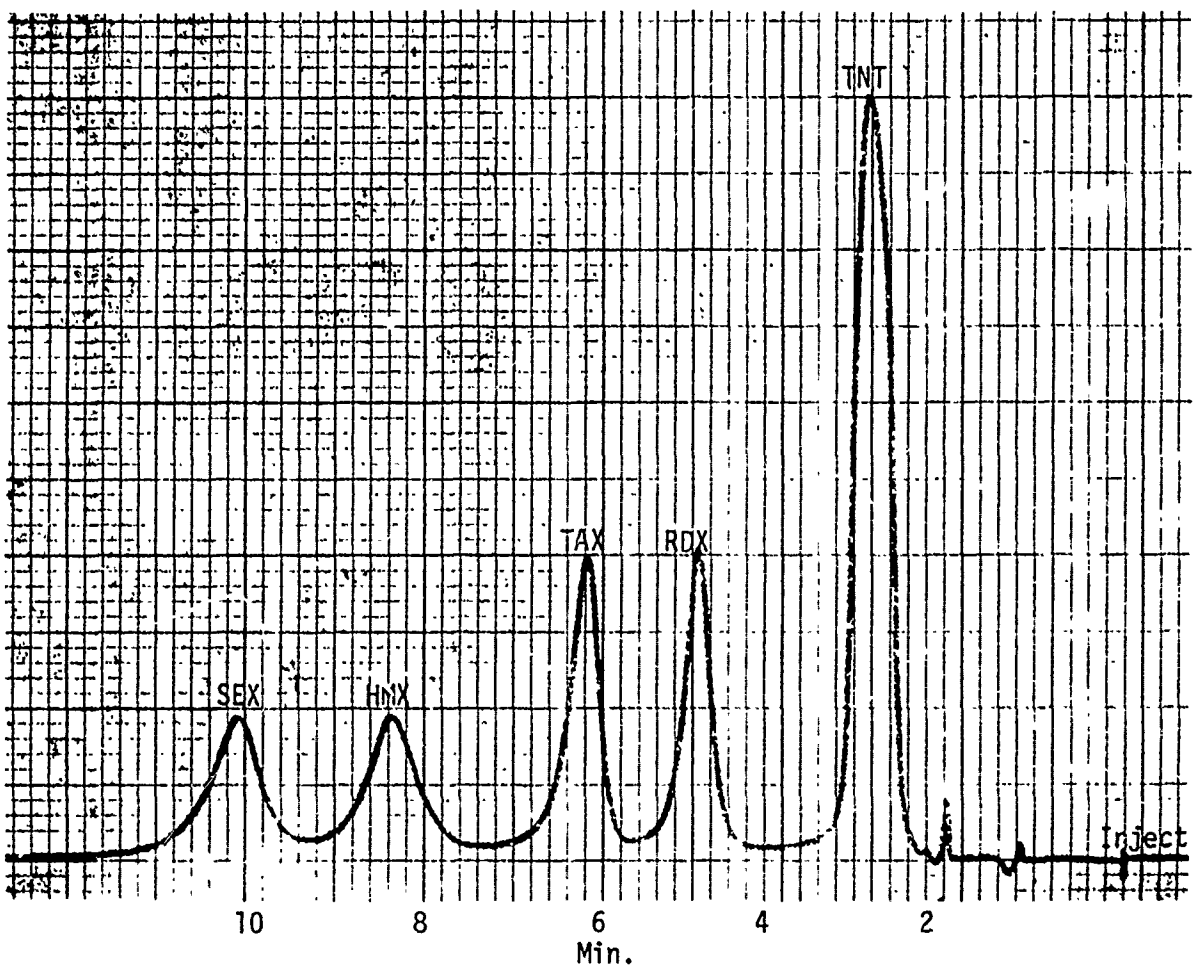
Date: 2-14-75 Operator:H.D.F.
Column No. 30 Length: 152.4 mm (6 in.)
I.D.: 2.1 mm (0.125 in.)
Column Packing: 5 micron Partasil
Mobile Phase and Gradient: Pump A-hexane; Pump B - 20% methanol, 30% acetonitrile, and 50% chloroform
Initial Condition: 0% Time: 3.6 k sec. (1.0 hr.)
Final Condition: 100%
Pressure: 1.406 M Pa (2000 PSI) Flow: 1.0 ml/60 sec.
Detector: UV, 254 nm Sensitivity: 08
Chart Speed: 5.1 mm/60 sec. (0.2 in./min.)
Gradient Curve: No. 7
Injection Amount: 10 microliters

Figure A-5. HPLC Chromatogram of HMX Dewater Solids



The above data was taken from Table A-4.

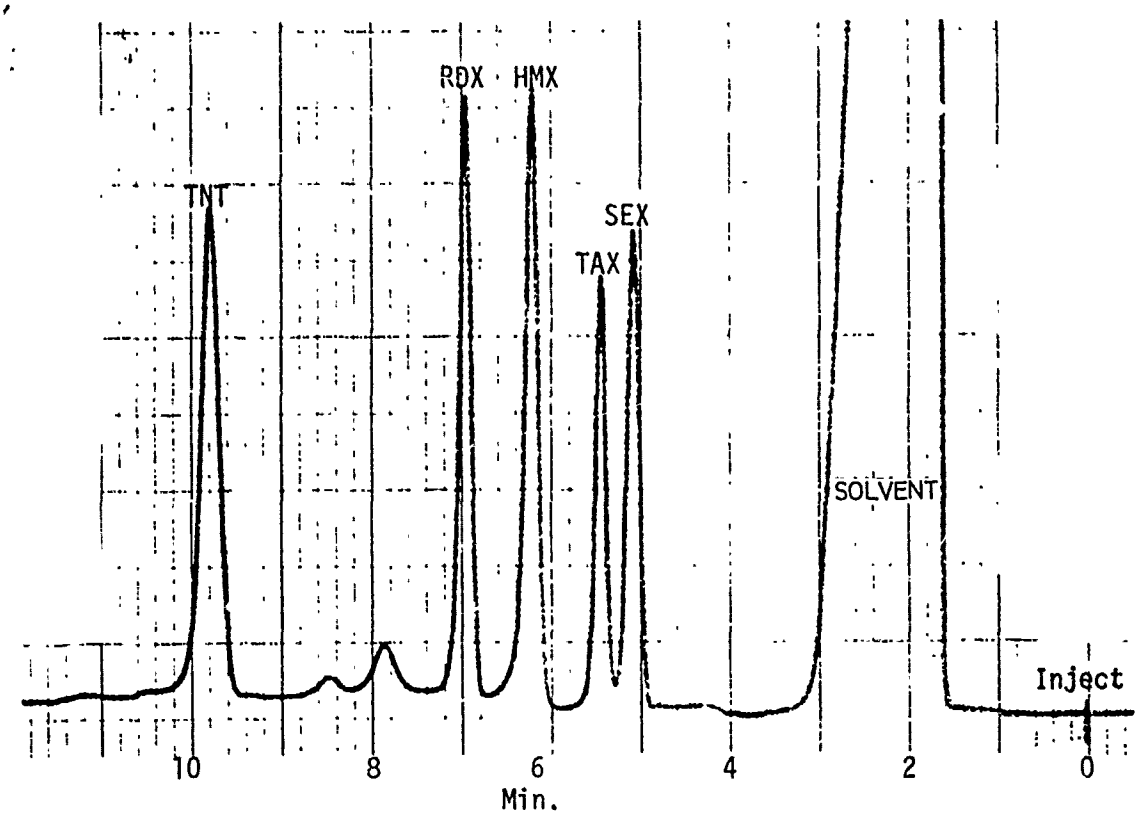
Figure A-6. Optimum Wavelength Determinations for Nitramines and TNT Micromeritics Chromomonitor 785



HPLC Instrument Parameters

Column: 30.5 cm x 6.4 mm (12 in. x 0.25 in.) stainless steel
Column Packing: LiChrosorb, 5μ MPS
Detector: UV at 245 nm
Mobile Phase: 5% Methanol, 10% acetonitrile, 15% chloroform, 70% isooctane
Flow Rate: 2.5 ml/min.
Injection Volume: 30 μl
Sample Concentration: 30 mg/l (each component)

Figure A-7. HPLC Chromatogram of Admixture - Normal Phase



HPLC Instrument Parameters

Column: 15.2 cm x 6.4 mm (6 in. x 0.25 in.) stainless steel
Column Packing: RP-8 LiChrosorb, 10 µmps
Mobile Phase and Gradient: A = water, B = Methanol: Acetonitrile (2:1)
0-40% B in 5 min.
Pressure: 1500 psi
Flow Rate: 3.0 ml/min.
Detector: UV at 230 nm; sensitivity = 0.10 AUFS
Injection Volume: 700 µl
Concentration: 1 mg/l (each component)

Figure A-8. HPLC Chromatogram of Aqueous Admixture Reverse Phase, Direct Injection

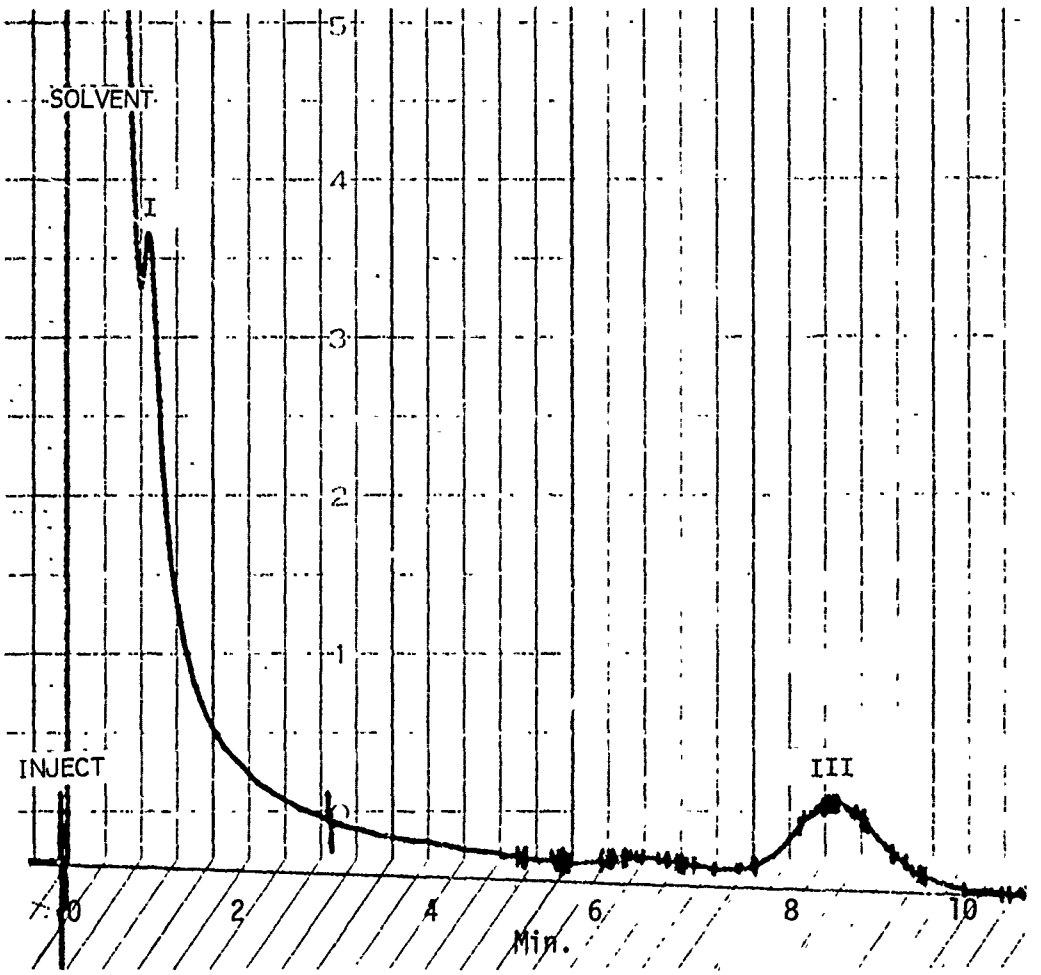


Figure A-9. GC Chromatogram of Cyclohexanone Related Compounds

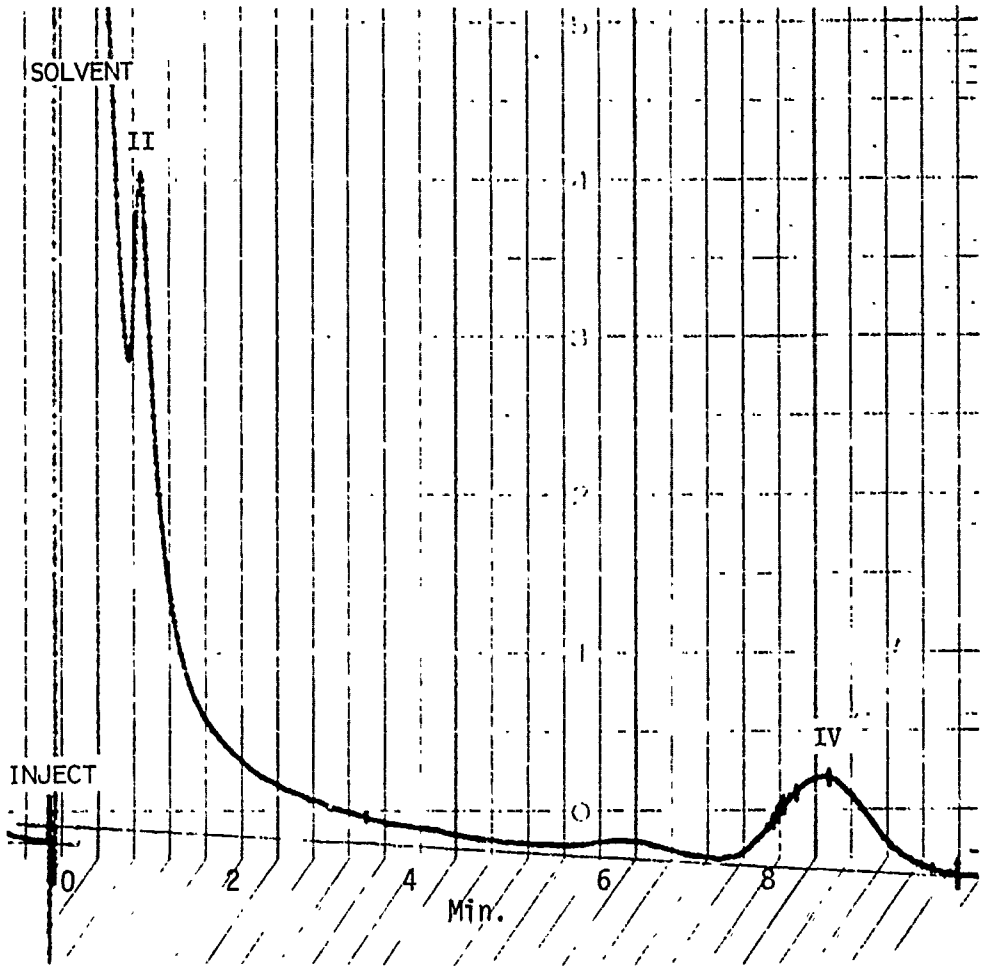


Figure A-10. GC Chromatogram of Cyclohexanone Related Compounds

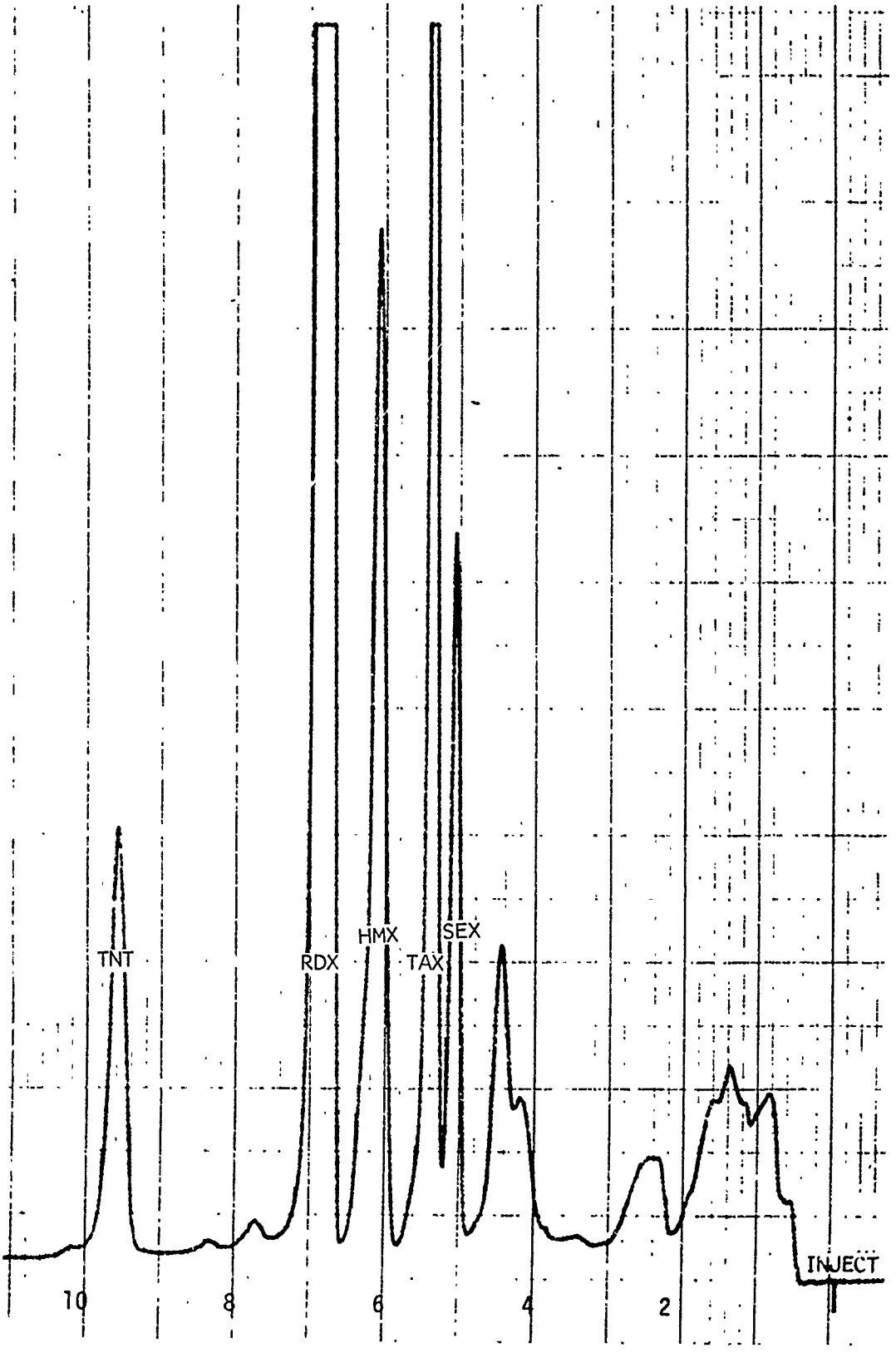


Figure A-11. HPLC Chromatogram of Typical Sample from HSAAP Effluent - Sample Point No. 3

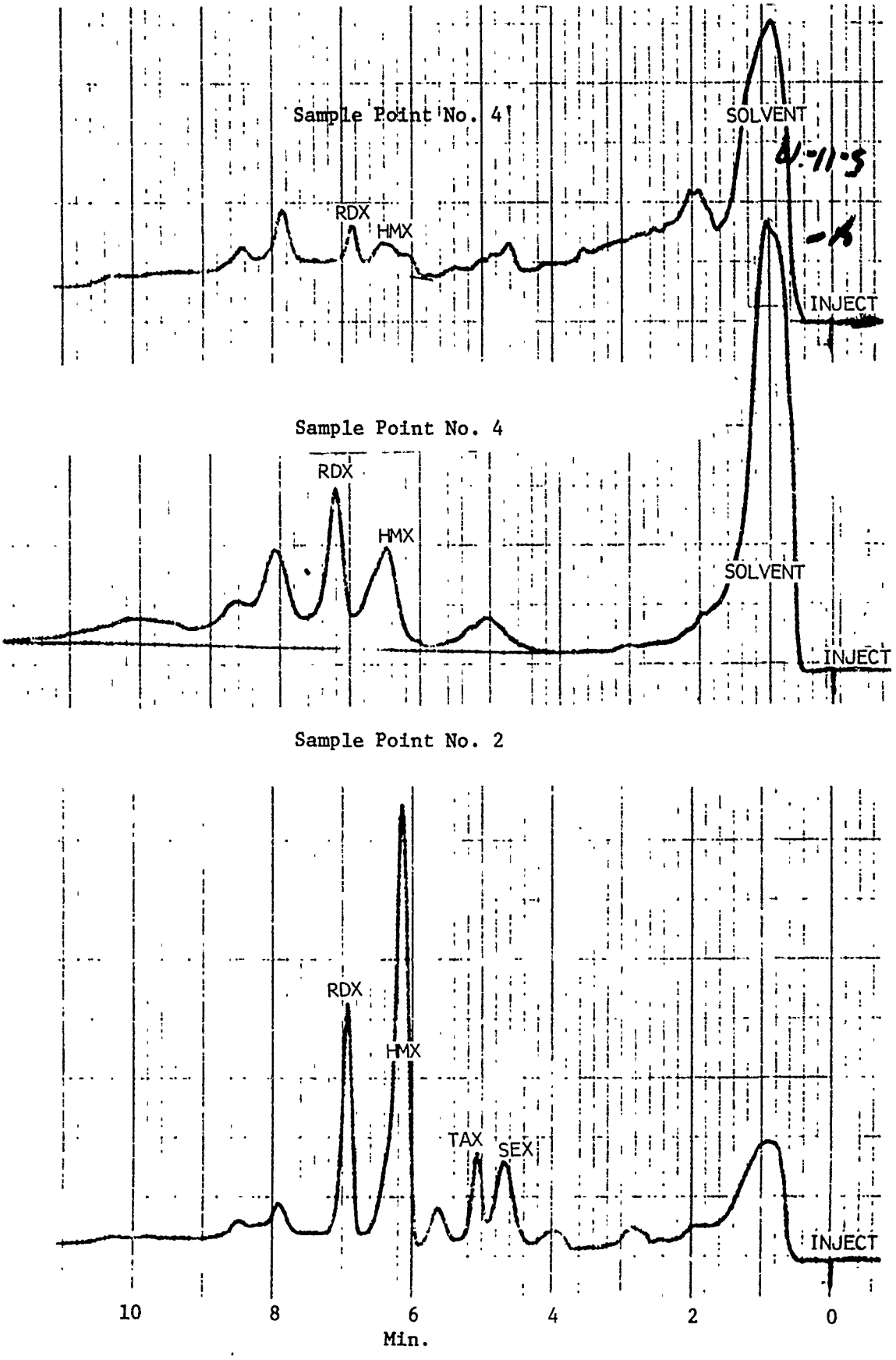


Figure A-12. HPLC Chromatograms of Typical Samples from HSAAP Effluents

Table A-1

RDX and HMX Dewater Fractions

Infrared Analyses - Results (HDC Personnel)

Sample		Remarks
RDX Dewater		
ES-1*		$(NH_4)_2SO_4$? + unidentified component
ES-2		$(NH_4)_2SO_4$? + unidentified component
ES-3		Insufficient sample
ES-4		Insufficient sample
ES-5		$(NH_4)_2SO_4$? + unidentified component
ES-6		Unidentified component - appears organic
ES-7		$(NH_4)_2SO_4$? + unidentified component
ES-8		$(NH_4)_2SO_4$? + RDX + unidentified component
ES-9		Single component, similar to, but not SEX
ES-10		$(NH_4)_2SO_4$? + unidentified component
ES-11		$(NH_4)_2SO_4$? + unidentified component
ES-12		Primarily SEX, some RDX, and unidentified component
ES-13		4 unidentified components
HMX Dewater**		
ES-7	1	Insufficient for characterization - organic; not explosive
	2	Unidentified. Same as H-7, ES-9.
ES-6	3	Unidentified; may be mixture of ES-7, 1 & 2.
	4	Unidentified; similar to ES-6, 3; ES-7, 2 present.
	5	Impure RDX
ES-8	6	Unidentified; same as ES-7, 2.
	7	Unidentified; resembles RDX and ES-7, 2.

*ES = solids obtained using a rotary vacuum evaporator; 1 = first fraction, 2 = second fraction, etc., eluted from liquid chromatograph during fractionation of components.

** = Only 3 fractions analyzed due to expenditure of funds. Fractions ES-7, ES-6 and ES-8 were refractionated into fractions 1, 2, 3, etc.

Table A-2

Reference Compounds Sent to E. I. DuPont Analytical and Physical Measurements Services and Midwest Research Institute

H-16, $C_{11}H_{19}N_7O_{11}$

1,9-diacetoxypentamethylene-4-acetyl-2,6,8-trinitrotetramine

H-6, $C_9H_{16}N_4O_2$, 2,6-diacetylpentamethylenetetramine

DNPT (or DPT) $C_5H_{10}N_6O_4$

2,6-dinitro(bicyclo)pentamethylenetetramine

AcAn, $C_9H_{16}N_8O_{12}$

1,9-diacetoxypentamethylene-2,4,6,8-tetranitramine

Compound "C", Structure not known.

BSX, $C_8H_{14}N_6O_{10}$

1,7-diacetoxytetramethylene-2,4,6-trinitramine

PHX, $C_7H_{13}N_7O_8$

1-(N)-methylolacetate-3,5,7-trinitro cyclotetramethylene tetramine

H-2, $C_9H_{18}N_6O_4$

1-acetamido-methyl hexamine-1-nitrate

PHX-AN, No Information

RDX, $C_3H_6N_6O_6$ cyclotrimethylenetrinitramine

HMX, $C_4H_8N_8O_8$ cyclotetramethylenetetranitramine

SEX, $C_6H_1N_7O_7$, octahydro-1-(N)-acetyl-3,5,7-trinitro-1,3,5,7-tetrazine

*HAMN, $C_6H_{13}N_5O_3$, hexamethylenetetramine mononitrate

*"106", $C_5H_{10}N_{10}O_{14}$, 1,9-Dinitroxy-2,4,6,8=tetranitro-2,4,6,8-tetraazanonane

*TTP, $C_2H_6N_6O_6$, 1,3,5-trinitro-1,3,5-triazapentane

*HADN, $C_6H_{14}N_6O_6$, hexamethylenetetramine dinitrate

* Sent to Midwest Research Institute only.

Table A-3

Compounds Identified by DuPont Analytical Services

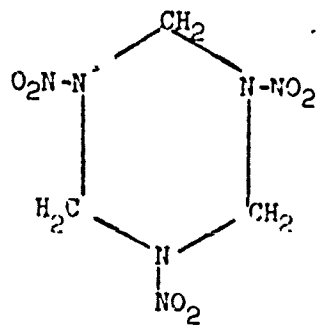
RDX

IUPAC Nomenclature

Hexahydro-1,3,5-trinitro-1,3,5-triazine

Chemical Nomenclature

Cyclotrimethylenetrinitramine



Molecular Formula

$C_3H_6O_6N_6$

Molecular Weight

222.13

Melting Point

204.1°C

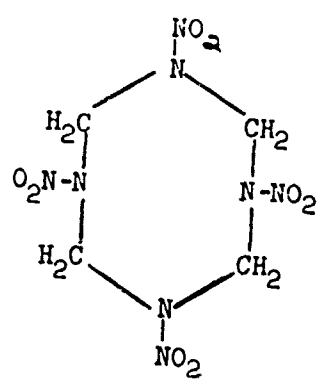
HMX

IUPAC Nomenclature

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine

Chemical Nomenclature

Cyclotetramethylenetetranitramine



Molecular Formula

$C_4H_8O_8N_8$

Molecular Weight

296.17

Melting Point

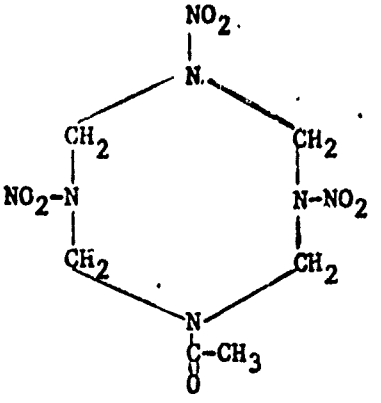
280°C

Table A-3 (continued)

SEX

IUPAC Nomenclature

Octahydro-1-(N)-acetyl-3,5,7-trinitro-1,3,5,7-tetrazine



Molecular Formula

$C_6H_{11}O_7N_7$

Molecular Weight

293.21

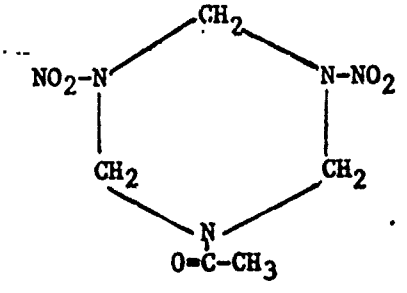
Melting Point

224.2 - 224.7°C

TAX

IUPAC Nomenclature

hexahydro-1-(N)-acetyl-3,5,-dinitro-1,3,5-triazine



Molecular Formula

$C_5H_9O_5N_5$

Molecular Weight

219.17

Melting Point

156°C

Reference

Basseler, Gerald Clayton, "The Chemistry of Cyclonite", National Defense Research Committee of the Office of Scientific Research and Development, Division 8 Informal Report, October, 1943.

Table A-4

Optimum Wavelength Determinations for Nitramines and TNT
Micromeritics Chromonitor 785

	Peak Area, Counts						
Wavelength,nm	TNT	RDX	HMX	BSX	AcAn	TAX	SEX
235	27,488	22,416	37,045	15,024	17,319	10,699	5,622
240	30,898	32,901	40.883	14,782	20,189	20,336	24,915
245	33,465	30.896	38,226	13,452	27,055	16,698	33,684
250	32,794	28,825	25,680	10,090	17,589	17,828	16,123
254	32,074	26,220	23,531	8,842	14,247	15,525	15,132
260	26,148	20,731	11,653	4,853	8,155	13,434	14,917
270	18,861	10,645	5,927	2,343	3,538	5,858	3,792
280	11,187	4,444	ND	669	1,040	1,998	1,139

	Normalized, Counts						
	TNT	RDX	HMX	BSX	AcAn	TAX	SEX
235	82.14	68.13	90.61	100.00	64.01	52.61	16.69
240	92.33	100.00	100.00	98.39	74.62	100.00	73.97
245	100.00	93.91	93.50	89.54	100.00	82.11	100.00
250	97.99	87.61	62.81	67.16	65.01	87.67	47.87
254	95.84	79.69	57.56	58.85	52.66	76.34	44.92
260	78.14	63.01	28.50	32.30	30.14	66.06	44.29
270	56.36	32.35	14.50	15.60	13.08	28.81	11.26
280	33.43	13.51	0.00	4.45	3.84	9.82	3.38

Table A-5

Analysis of Standard Solutions
HPLC and Concentration

Mixture No.		Concentration, Milligrams/Liter RDX	HMX	SEX	TAX	TNT
7	Added	0.50	1.00	4.00	8.00	12.00
	Found 1	0.15	0.98	3.33	6.66	9.84
	Found 2	0.41	0.77	3.17	6.44	9.32
8	Added	1.00	16.00	12.00	4.00	8.00
	Found 1	1.11	13.10	9.48	4.20	6.73
	Found 2	1.35	10.64	11.20	3.72	6.49
9	Added	4.00	12.00	8.00	0.50	16.00
	Found 1	3.57	9.06	5.60	0.35	10.69
	Found 2	3.21	8.61	5.71	0.38	10.03
10	Added	8.00	4.00	16.00	1.00	0.50
	Found 1	6.76	4.44	10.61	0.52	ND*
	Found 2	6.76	3.01	11.85	0.51	0.07
11	Added	12.00	0.50	1.00	16.00	4.00
	Found 1	10.55	0.47	0.74	11.95	1.48
	Found 2	7.91	0.01	0.56	8.42	1.09
12	Added	16.00	8.00	0.50	12.00	1.00
	Found 1	14.35	7.13	ND*	8.11	0.86
	Found 2	17.16	6.84	0.15	8.19	0.84

*None detected

Table A-6

Precision and Accuracy Determinations
HPLC Direct Injection

No.[1]	Found, Milligrams/Liter [1]				
	SEX	TAX	HMX	RDX	TNT
1	1.00	1.02	1.00	1.02	1.02
2	1.03	1.06	1.19	1.19	1.02
3	1.04	1.05	1.18	1.24	1.03
4	0.99	0.97	1.01	1.07	1.00
5	1.06	0.98	1.04	1.10	1.00
6	1.10	0.96	1.10	1.04	1.02
7	1.05	0.94	1.09	1.22	0.96
8	1.05	0.95	1.21	1.02	0.93
9	1.04	1.01	1.20	1.03	0.97
10	1.16	0.89	1.12	1.18	1.03
11	0.98	1.00	0.96	1.05	1.03
Precision	0.05	0.05	0.08	0.08	0.03
Accuracy[2]	0.04	-0.04	0.09	0.08	-0.02

1. The sample contained the five components at 1 mg/l.
2. Accuracy = Found minus Known

Table A-7

Precision and Accuracy Determinations
HPLC Direct Injection

No.[1]	Found, Milligrams/Liter[1]				
	SEX	TAX	HMX	RDX	TNT
1	6.00	6.12	6.00	6.12	6.12
2	5.78	5.77	5.56	5.34	5.60
3	6.36	5.84	6.03	5.65	6.17
4	6.25	5.33	6.03	5.65	5.79
5	5.83	6.01	5.60	5.70	6.17
6	6.24	5.81	5.94	5.51	6.14
7	6.40	5.50	5.93	5.25	5.73
8	6.53	5.66	5.69	5.47	6.18
9	6.00	5.04	5.82	5.92	6.11
10	6.14	5.14	5.76	5.21	5.87
11	6.02	5.15	5.80	5.41	6.28
Precision	0.24	0.35	0.16	0.28	0.23
Accuracy[2]	0.14	-0.63	-0.17	-0.55	-0.11

1. The solution contained each component at 6 mg/l
2. Accuracy = Found minus Known

Table A-8

Precision and Accuracy Determinations
HPLC Direct Injection

No.[1]	Found, Milligrams/Liter[1]				
	SEX	TAX	HMX	RDX	TNT
1	10.00	10.20	10.00	10.20	10.20
2	8.70	10.18	9.50	10.28	10.26
3	10.35	10.57	10.20	10.95	10.54
4	9.48	10.83	10.25	10.57	11.62
5	9.66	10.61	10.22	12.35	9.90
6	10.51	10.85	10.05	10.50	10.60
7	11.15	10.81	10.62	11.00	10.74
8	8.23	9.98	9.34	10.09	10.40
9	9.99	9.66	9.85	9.75	10.19
Precision	0.90	0.42	0.39	0.76	0.49
Accuracy[2]	-0.22	0.21	0.00	0.43	0.29

1. The sample contained the five components at 10 mg/l.
2. Accuracy = Found minus Known

Table A-9

Precision and Accuracy Determinations
HPLC-Direct Injection

No.[1]	Found, Micrograms/Liter[1] SEX	TAX	HMX	RDX	TNT
1	50.0	50.0	50.2	50.8	50.6
2	40.9	38.9	57.4	50.8	42.2
3	31.8	38.9	53.8	53.8	50.6
4	36.4	38.9	71.7	59.8	50.6
5	36.4	44.4	64.5	56.8	50.6
6	40.9	50.0	61.0	53.8	50.6
7	40.9	38.9	78.9	53.8	59.3
8	45.5	44.4	75.3	56.8	59.3
9	50.0	50.0	64.5	53.8	50.6
10	40.9	44.4	64.5	59.8	50.6
Precision	5.8	4.9	9.2	3.2	4.9
Accuracy[2]	-8.6	-6.1	13.9	4.2	0.9

1. The solution contained the five components at 50 µg/ml
2. Accuracy = Found minus Known

Table A-10

Precision and Accuracy Determinations
HPLC Direct Injection

No.[1]	Found, Micrograms/Liter[1]				
	SEX	TAX	HMX	RDX	TNT
1	200.0	200.0	200.8	203.2	202.4
2	175.8	225.0	225.9	193.3	236.1
3	175.8	187.5	175.7	203.2	191.2
4	175.8	181.3	185.7	198.2	213.6
5	175.8	187.5	175.7	208.2	202.4
6	181.9	200.0	185.7	203.2	202.4
7	187.9	200.0	190.8	193.3	202.4
8	181.9	187.5	210.8	223.0	202.4
9	200.0	206.3	205.8	208.2	213.6
10	181.9	187.5	180.7	203.2	202.4
Precision	9.6	12.9	16.6	8.6	12.1
Accuracy	-15.4	-3.7	-6.2	0.5	3.6

1. The solutions contained the five components at 200 µg/ml.
2. Accuracy = Found minus Known

Table A-11

Analysis of Standard Solutions
HPLC Direct Injection

Mixture No.	Concentration, mg/liter RDX	HMX	SEX	TAX	TNT
No. 7 Added	0.51	1.00	4.00	8.13	1[illegible]
Found 1	0.73	1.09	4.10	8.16	[illegible]25
Found 2	0.87	1.36	4.10	8.16	11.46
No. 8 Added	1.02	16.06	12.00	4.02	8.10
Found 1	1.51	14.08	12.71	4.21	8.23
Found 2	1.48	13.38	11.90	4.23	8.49
No. 9 Added	4.06	12.04	8.00	0.51	16.19
Found 1	4.25	9.56	9.41	- *	14.27
Found 2	4.03	9.10	8.90	- *	13.80
No. 10 Added	8.13	4.02	16.00	1.02	0.51
Found 1	7.53	4.11	17.03	0.34*	0.57
Found 2	7.95	4.42	18.75	- *	0.50
No. 11 Added	12.19	0.50	1.00	16.26	4.05
Found 1	10.55	- *	0.96	15.20	3.89
Found 2	10.22	- *	0.67	15.50	3.87
No. 12 Added	16.26	8.03	0.50	12.19	1.01
Found 1	13.76	4.93	0.38	10.52	1.13
Found 2	13.15	4.22	0.22	10.62	0.81

*These components were masked at this concentration due to the high concentration of the component eluting immediately prior to t m. Elution order was: SEX; TAX; HMX; RDX; and TNT.

Statistical Evaluation

	RDX	HMX	SEX	TAX	TNT
Precision (Range Method)[10]	0.258	0.434	0.515	0.093	0.193
Precision (D^2 Method)[11]	0.246	0.371	0.576	0.112	0.191
Average Difference	-0.696	-1.338	0.512	-0.575	-0.475
Standard Deviation of Difference	1.320	1.724	0.839	0.851	0.892
Standard Error	0.539	0.771	0.342	0.426	0.364

Table A-12

Analysis of Standard Solutions
HPLC Direct Injection

Mixture No.		Concentration, Micrograms/Liter RDX	HMX	SEX	TAX	TNT
1	Added 1	25.4	50.2	100.0	203.2	10.1
	Found 1	35.0	42.0	138.4	220.7	ND
	Found 2	35.0	42.0	112.1	186.8	ND
2	Added	50.8	100.4	200.0	10.2	25.3
	Found 1	39.5	70.1	191.2	ND	74.9
	Found 2	43.9	84.1	197.8	ND	56.2
3	Added	101.6	200.8	10.0	25.4	50.6
	Found 1	96.5	112.1	ND	ND	93.7
	Found 2	87.7	126.1	ND	ND	93.7
4	Added	203.2	10.0	25.0	50.8	101.2
	Found 1	171.0	ND	26.4	45.1	131.2
	Found 2	171.0	ND	32.9	45.1	112.4
5	Added	10.2	25.1	50.0	101.6	202.4
	Found 1	ND	14.1	59.3	101.9	224.9
	Found 2	ND	14.1	65.9	96.2	224.9
		Statistical Evaluation				
Precision (Range Method)[10]		3.9	8.3	10.2	16.7	8.3
Precision (D^2 Method)[11]		3.8	8.1	10.1	15.6	9.4
Average Difference		-11.9	-37.7	9.2	6.0	31.6
Standard Deviation of Difference		14.7	38.8	13.0	12.2	11.7
Standard Error		7.4	22.4	6.5	7.0	5.9
Lower Detection Limit[8]		34.7	63.4	23.7	52.0	60.8

Table A-13

Cyclohexanone Related Compounds
Gas Chromatographic Analysis

Compound					
I	Concentration, mg/l	83.0	41.5	20.7	10.3
	Peak Height, mm	90	49	33	17
II	Concentration, mg/l	86.0	43.0	21.5	5.1
	Peak Height, mm	97	45.5	21	0
III	Concentration, mg/l	207.5	83.0	41.5	20.7
	Peak Height, mm	12.5	5.5	1.5	0
IV	Concentration, mg/l	215.0	86.0	43.0	21.5
	Peak Height, mm	15.0	5.5	2.0	0

Lower Detection Limits, mg/l

I	2-hydroxymethylcyclohexanone (Compound I) = 18.9
II	spiro 1-oxocyclohexane - 2,2',3',4',5',6',7',8', hexahydrobenzo [b] pyran (Compound II) = 3.7
III	2-(2-cyclohexenyl) cyclohexanone (Compound III) = 68.2
IV	2-(1-cyclohexenyl) cyclohexanone (Compound IV) = 21.8

Table A-14

Wastestream Monitor-Nitramines and TNT
HPLC-Direct Injection

Sample Point Number 2

Date	SEX	TAX	Concentration, mg/l HMX	RDX	TNT	pH
5-10 & 11-79	0.32	0.49	1.13	0.83	ND*	6.60
5-16 & 17-79	0.70	ND	1.91	2.50	ND	6.70
5-22 & 23-79	1.80	0.23	1.22	2.19	ND	6.81
5-29 & 30-79	1.24	0.45	1.54	0.63	ND	7.10
6-5 & 6-79	1.40	0.17	1.78	4.41	ND	6.71
6-12 & 13-79	0.95	0.31	1.25	2.97	ND	7.12

Sample Point Number 3

Date	SEX	TAX	Concentration, mg/l HMX	RDX	TNT	pH
5-10 & 11-79	1.56	4.50	1.95	16.02**	1.40	3.40
5-16 & 17-79	1.70	2.41	3.36	9.74	0.77	6.90
5-22 & 23-79	1.06	2.54	1.54	5.45	0.21	7.20
5-29 & 30-79	1.44	0.74	1.97	15.47**	1.38	7.30
6-5 & 6-79	1.34	4.27	2.08	8.53	0.22	6.94
6-12 & 13-79	2.03	5.24	2.95	6.43	2.01	7.29

**High values attributed to spillage of RDX/wax caused by malfunction of the deluge system at Building I-1 on these dates.

Table A-14 (continued)

Sample Point Number 4

Date	SEX	Concentration, µg/l TAX	HMX	RDX	TNT	pH
5-10 & 11-79	ND	ND	90	110	ND	6.50
5-16 & 17-79	30	10	170	340	10	6.90
5-22 & 23-79	ND	ND	144	609	ND	7.32
5-29 & 30-79	ND	ND	160	240	ND	7.40
6-5 & 6-79	40	ND	190	360	ND	7.22
6-12 & 13-79	ND	ND	210	330	ND	7.35

Sample Point Number 4'

Date	SEX	Concentration, µg/l TAX	HMX	RDX	TNT	pH
5-10 & 11-79	ND	ND	99	39	ND	6.60
5-16 & 17-79	ND	ND	67	53	ND	7.20
5-22 & 23-79	ND	ND	23	20	ND	7.32
5-29 & 30-79	ND	ND	194	215	ND	7.50
6-5 & 6-79	ND	ND	10	58	ND	7.39
6-12 & 13-79	ND	ND	40	22	ND	7.52

**ND = None Detected

Table A-15

Operating Production Buildings[a]

Date	B	C	D	E	G	H	I	J	K	L	M	N	O
May 10-11	3	3	3 6	3 6	4 5 6	4 5	1	3	3 5		3 5 6	2 3 5 6	3 5
May 16-17	3	3	3 6	3 6	4 5 6	4 5	6	3	3 5	6	3 6	2 3	3 5
May 22-23	3	3	3 6	3 6	4 5 6	4 5	6	3	3 5		3 6	2 3 6	3 5
May 29-30	3	3	3 6	3 6	4 5 6	4 5	6 1	3	3		3 6	3 5 6	3 5
June 5-6	3	3	3 6	3 6	4 5 6	4 5		3	3 5		3	2 3 6	3 5
June 12-13	3	3	3 6	3 6	4 5 6	4 5		3	3 5		3 5	2 3 5	3 5

[a] Letters on column heads refer to the types of buildings, numbers to the production line. Thus number 5 in Column G refers to Building G-5.

Table A-16

Flows and Explosives Concentrations Wastestreams and Holston River

Date	Flow* Holston River (4')	Point 2	Point 3	Point 4
5-22 & 23-79	2999.56 CFS	0.99	2.66	1.15
5-29 & 30-79	3676.90 CFS	0.99	1.97	1.12
6-5 & 6-79	3536.65 CFS	0.92	1.37	1.33
6-12 & 13-79	3447.45 CFS	0.92	1.08	0.96
Average of 4	3415.14 CFS	0.955	1.77	1.14
	Explosive Concentration and Mass			
HMX ($\bar{X}_4$), mg/l	0.067	1.45	2.14	0.176
RDX ($\bar{X}_4$), mg/l	.079	2.55	8.97	0.385
SEX ($\bar{X}_4$), mg/l		1.35	1.47	0.10
TAX ($\bar{X}_4$), mg/l		0.29	3.20	0.00
TNT ($\bar{X}_4$), mg/l		0.00	0.95	0.00
RDX lb/day		20.32	132.48	3.66
HMX lb/day		11.55	31.61	1.67
SEX lb/day		10.73	21.66	0.95
TAX lb/day		2.31	47.15	0.00
TNT lb/day		0.00	14.00	0.00

*Flow in million gallons per day except as noted.

Table A-17

Multiple Analyses of Monitor Samples Taken 5-10 & 11-79
HPLC - Direct Injection

Sample Point	Date Analyzed	Concentration, mg/l				
		SEX	TAX	HMX	RDX	TNT
2	5-11-79	0.32	0.49	1.13	0.83	ND*
2	5-25-79	0.31	0.23	1.15	0.57	ND
2	6-1-79	0.42	0.23	1.43	0.47	ND
2	6-18-79	0.32	0.23	0.62	0.28	ND
3	5-11-79	1.56	4.50	1.95	16.02	1.40
3	5-25-79	1.59	5.16	2.25	15.56	1.20
3	6-1-79	1.60	4.39	3.33	18.16	2.04
3	6-18-79	1.46	3.93	3.11	16.13	0.54
4	5-11-79	ND	ND	0.09	0.11	ND
4	5-25-79	ND	ND	0.15	0.31	ND
4	6-1-79	ND	ND	0.25	0.37	ND
4	6-18-79	ND	ND	0.22	0.06	ND
		Concentration, µg/l				
4'	5-11-79	ND	ND	99.0	39.2	ND
4'	5-25-79	ND	ND	39.1	42.2	ND
4'	6-1-79	ND	ND	96.9	67.7	ND
4'	6-18-79	ND	ND	60.9	35.5	ND

* None Detected (Refer to Table A-12 for lower detection units).

Table A-18

Wastestream Monitor-Gas Chromatographic Analysis

Sample Point 2			Sample Point 3		
Date	Concentration, mg/l I or II[1,2]	III or IV[1]	Date	Concentration, mg/l I or II[1,2]	III or IV[1]
5-10 & 11-79	17.6	ND	5-10 & 11-79	24.7	ND
5-16 & 17-79	19.4	ND	5-16 & 17-79	22.4	ND
5-22 & 23-79	16.3	ND	5-22 & 23-79	19.4	ND
5-29 & 30-79	26.9	ND	5-29 & 30-79	25.8	ND
6-5 & 6-79	23.8	ND	6-5 & 16-79	20.1	ND
6-12 & 13-79	24.5	ND	6-12 & 13-79	24.5	ND

Sample Point 4			Sample Point 4'		
Date	Concentration, mg/l I or II[1,2]	III or IV[1]	Date	Concentration, mg/l I or II[1,2]	III or IV[1]
5-10 & 11-79	20.1	ND	5-10 & 11-79	23.2	ND
5-16 & 17-79	23.8	ND	5-16 & 17-79	10.3	ND
5-22 & 23-79	24.1	ND	5-22 & 23-79	34.8	ND
5-29 & 30-79	26.9	ND	5-29 & 30-79	28.0	ND
6-5 & 6-79	27.6	ND	6-5 & 6-79	24.5	ND
6-12 & 13-79	27.5	ND	6-12 & 13-79	23.8	ND

1. I = 2 hydroxymethylcyclohexanone
   II = spiro [1-oxocylohexanone-2,^{1}-3^{1},4^{1},5^{1},6^{1},7^{1},8^{1} - hexahydrobenza[b] pyran]
   III = 2-(2-cyclohexenyl) cyclohexanone
   IV = (1-cyclohexenyl) cyclohexanone

2. Concentration reported as Compound I

Table A-19

Optimum Sample Injection Volume Determinations and Detection Limits for RDX and HMX

Injection No. (50µl[a])	Component	Response (Area Counts)
	28.5 mg/l HMX; 17.6 mg/l RDX	
1	RDX	23,691
	HMX	49,899
2	RDX	26,252
	HMX	52,220
3	RDX	20,900
	HMX	64,668
4	RDX	27,670
	HMX	65,310
	11.0 mg/l HMX; 11.4 mg/l RDX	
1	RDX	15,975
	HMX	47,651
2	RDX	15,058
	HMX	32,387
3	RDX	13,270
	HMX	4,168
4	RDX	11,686
	HMX	19,748
	5.7 mg/l HMX; 3.5 mg/l RDX	
1	RDX	5,243
	HMX	6,527
2	RDX	4,204
	HMX	9,682
3	RDX	3,483
	HMX	7,679
4	RDX	4,983
	HMX	8,693

(Table A-19 continued)

Injection No. (50 µl[b])	Component	Response (Area Counts)
	28.5 mg/l HMX; 17.6 mg/l RDX	
1	RDX	13,482
	HMX	34,281
2	RDX	12,756
	HMX	29,986
3	RDX	12,094
	HMX	28,190
4	RDX	11,810
	HMX	33,541
	11.4 mg/l HMX; 11.0 mg/l RDX	
1	RDX	8,033
	HMX	14,025
2	RDX	8,920
	HMX	10,641
3	RDX	8,412
	HMX	15,131
4	RDX	7,381
	HMX	13,335
	5.7 mg/l HMX; 3.5 mg/l RDX	
1	RDX	2,072
	HMX	4,590
2	RDX	2,730
	HMX	3,093
3	RDX	2,891
	HMX	2,805
4	RDX	1,640
	HMX	3,799

[a] Component peaks were wide with considerable "tailing".
[b] Component peaks were much "sharper" with very little "tailing".

APPENDIX B

Separation and Analysis of RDX and HMX Dewater Solids

Alton F. Dahl

E. I. duPont de NeMours and Company (Inc.)

(A report prepared for Holston Defense Corporation, Operating Contractor, Holston Army Ammunition Plant)

Page Nos. 54 through 77 of
Technical Report HDC-51-79

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ANALYTICAL OR PHYSICAL MEASUREMENTS SERVICE REPORT

Customer's Reference: P.O. #105-0011	Du Pont No. 754-81
	Date Received 6/19/75

SEPARATION AND ANALYSIS OF RDX AND HMX DEWATER SOLIDS
(YOUR JOB NO. 84-3513

SUMMARY

The title samples were received June 19, 1975. The acetonitrile soluble portions of each were fractionated by Liquid Chromatography (LC). The major individual fractions were isolated and characterized by infrared (IR) and nuclear magnetic resonance (NMR) utilizing Fourier Transform (FT) techniques because of the small amount of sample. LC retention times were also determined on reference standards where available.

From the RDX Dewater solids, we have identified RDX itself and TAX, the monoacetyl dinitro derivative. A third major fraction, which may be a mixture, was found to contain N-acetyl and probably C-ONO_2 functions, with a cyclic backbone. Positive identification could not be made.

From the HMX dewater solids, we have identified RDX and SEX, the monoacetyl dinitro derivative of HMX. There were also several minor constituents in both samples, upon which very little characterization was performed.

Alton V. Dahl 12/15/75
Signed Date

(Continued on Page 2)

We also received an ether extracted filtered water sample (apparently mislabeled "ether extract") and an ether blank. No significant components were detected in either of these.

DISCUSSION

The total package which we received from Holston Defense Corporation, in addition to the four samples, included liquid chromatographic scans of the four, a list of related compounds, IR and NMR scans, and a set of twelve reference standard samples.

I. Liquid Chromatography

The samples of freeze-dried dewater solids were supplied suspended in a small quantity of water. To prepare a sample for analysis we removed an aliquot containing visually representative portions of solid and liquid, evaporated it to dryness at <40°C with a stream of nitrogen and weighed it. Acetonitrile was added to the residue and the mixture was allowed to stand overnight. The supernatant liquid was carefully decanted and the residue washed into the extract with a second portion of acetonitrile, dried and reweighed. For injection into the LC instrument, the concentration of the solution was adjusted to 2%.

A Du Pont Model 830 Liquid Chromatograph was used with a 20" x 1/4" OD Zorbax® SIL column, 1800 psi inlet pressure, solvent flow 0.2 ml./min. Primary mobile phase was n-hexane, the secondary was 20 volume % methanol, 30% acetonitrile, 50% chloroform (special "distilled in glass" grades of each). Gradient elution was used at 1%/minute from 0 to 100% secondary. The injection sample loop had a volume of 0.25 ml. An ultraviolet detector (254 nm) was employed. Samples were taken exit the detector and evaporated under a stream of nitrogen at room temperature to give material for characterization. To provide sufficient amounts of material, three replicate chromatographic runs were made on each of the two Dewater samples, in addition to initial scouting tests to define chromatographic conditions.

Figure 1 is a hand-drawn composite chromatogram of each of the two samples, expanding the recorder attenuation to put all major peaks on a single scale for easy comprehension. On the plot is given our designations for identification of the major fractions. (The numbers correspond roughly to inches on the chart from injection.)

Chromatographic control tests included solvent blank runs (column effluents at about 40% secondary phase were analyzed as blanks for sample fractions. See Figure 2 for an IR solvent blank.) Reference standard samples of RDX and HMX were also chromatographed.

Infrared scan of the recovered material from the RDX column effluent (Figure 3) was indistinguishable from that of the standard. In this case, the amount of sample was sufficiently large that solvent background was not significant.

II. Characterization

Infrared scans were run on a Digilab FTS 14 (Fourier Transform) instrument with 100 repetitive scans per sample at double precision. Samples were prepared as micro KBr pellets. The figures included in this report are plotted on a conventional transmission scale, except Figure 2, which is on a linear absorbance basis.

Nuclear magnetic resonance (NMR) scans were run in dimethyl sulfoxide-d_6 solution on a 100 MHz ^1H Fourier Transform unit. Up to 500 repetitive scans were run per sample. Unfortunately, the instrument was not operating at maximum performance when the samples were analyzed. Subsequently, the instrument was inoperable for a period of several weeks, precluding the analysis of a second set of samples which we had prepared.

As a note of interpretation of the NMR scans in Figures 9-12, the intense peaks at 2.48 and 3.30 ppm are derived from proton-containing DMSO and water, respectively. The regularly spaced disturbances which occur about every 1.2 ppm and are most intense at 9.2 ppm are 60 cycle harmonics.

III. Identifications

The identification data on the various LC fractions are summarized in Table I.

Fractions "RDX-8" and "HMX-8": Retention times and characterization data for the two fractions were indistinguishable from each other. Identification was by comparison of retention time, IR and NMR spectra with those of the known standard. There is ample resolution in the IR spectra to exclude the presence of HMX as a major constituent. (Retention times and NMR spectra, however, are similar for the two compounds.)

Fractions "RDX-11" and "HMX-11": Both IR and NMR spectra of known SEX supplied by Holston agree closely with our observed spectra for "HMX-11."

Our IR scan for "RDX-11" is qualitatively close to that for "HMX-11," including an amide carbonyl band. Likewise our retention times were similar. However, there is just enough difference in IR fine structure to indicate an expected difference between an 8 and a 6-membered ring. No meaningful NMR spectra was obtained on "RDX-11." We had no reference spectra of TAX for comparison. Likewise we do not have standard samples of either of the two compounds.

In all the above four fractions, the concentrations of the compounds in the LC cuts were sufficiently low that bands from the solvent were evident. Attempts to calculate IR difference spectra between samples and solvent blanks suggested the possibility of some extraneous hydrocarbon contaminations.

Fraction "RDX-9": Figure 1 shows that this fraction, which predominates the RDX solids, has no counterpart in the HMX solids. The shoulder on the far side of the peak was found reproducible. For analysis, we cut off collection of fraction "9A" prior to the appearance of the shoulder. However, it is very possible that the fraction we examined contained more than one major constituent.

The NMR absorptions at 2.17, 5.63 and 6.13 ppm were reproducibly observed in two different NMR campaigns on two samples from different LC fractionations. We would assign the first to the acetyl group and one or both of the second two to methylenes adjacent to an $-ONO_2$ ester, by comparison with the spectrum supplied of ATX. The infrared scan shows a likely amide carbonyl at 1670 cm^{-1}, and contains a typical pattern of fine structure indicative of a cyclic molecule, with a window around 1100 cm^{-1} characteristic of RDX. Comparison of our IR scan for this material (Figure 5) with that for "RDX-11" (Figure 6) shows many similarities. (One must correct for the solvent background present in the latter which is not in the former.) There is a significant band at 1430 cm^{-1} in Figure 5 only. This might be the nitrate ester.

There are no apparent indications of NH_4^+ or NO_3^- in any of the fractions characterized.

IV. Miscellaneous

LC runs on the filtered water and ether blanks indicated no significant material to be present.

In preliminary scouting on LC instrument conditions, we found that installation of an extra length of column and reducing the gradient rate resulted in increased resolution.

Screening tests were run using a gel permeation (GPC) system, with Styragel® columns, and a THF mobile phase. THF soluble fractions of the solids samples were injected. Some separation was obtained. However, the resolution was not as good as in the above LC system. Both refractive index and UV detectors were used with noticeable difference in relative response of different peaks from the two detectors. From the RDX solids sample was isolated one predominant peak. NMR scan on this peak was similar to that for fraction "RDX-9A" above.

V. Suggestions for Future Work

We recommend that new samples of Dewater solids be obtained for future work on this project. There is only a small amount of each remaining and they have stood in water for over nine months.

Of highest priority for new work should be experiments aimed at separating "RDX-9" into its constituents. A quantity of this material would be isolated and chromatographed using different mobile phase/column combinations. We anticipate that the FT-NMR will be back in operation in the near future. This would facilitate characterization of the minor fractions which have to date been ignored.

It would be extremely useful to have additional characterization techniques. As our collective experience in nitramine chemistry is limited, we would best rely on you for suggestions. For example, is there any quantitative or qualitative wet chemistry to distinguish between an $N\text{-}NO_2$ and an $O\text{-}NO_2$ group, or to measure quantitatively and simultaneously oxidized and reduced forms of organic nitrogen? There are also alternative techniques that come to mind, for example polarography and chemical ionization mass spectrometry. Specific leads would be helpful here, otherwise a major methods development effort would be required.

*****

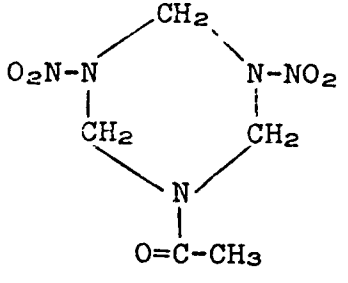
TABLE I

SUMMARY OF IDENTIFICATION DATA

Fraction Designation (A)	Identification	LC Retention Time Vs. Standard	Infrared Scan Figure No.	^{1}H NMR Figure No.	^{1}H NMR Peaks, ppm	Notes
RDX-8	RDX	Yes	4	-	6.08	
RDX-9A	-	-	5	9, 10	2.17, 5.63, 6.13	(B)
RDX-11	TAX	(C)	6	-	-	(D)
HMX-8	RDX	Yes	7	11	6.08	
HMX-11	SEX	(C)	8	12	2.19, 5.53, 5.95	
HMX-12	-	-	-	-	5.52	

Structures

TAX



SEX

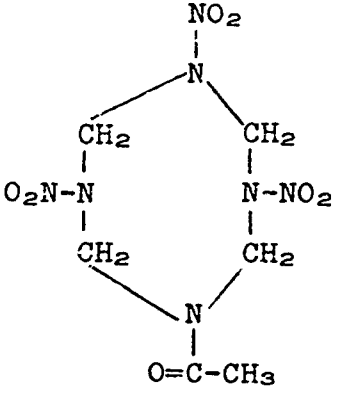


TABLE I NOTES

(A) See Figure 1. Numbers in designations derived from LC retention times.

(B) Fraction may contain more than one component.

(C) No standard samples available.

(D) No reference spectra available. Identified by comparison with HMX-11.

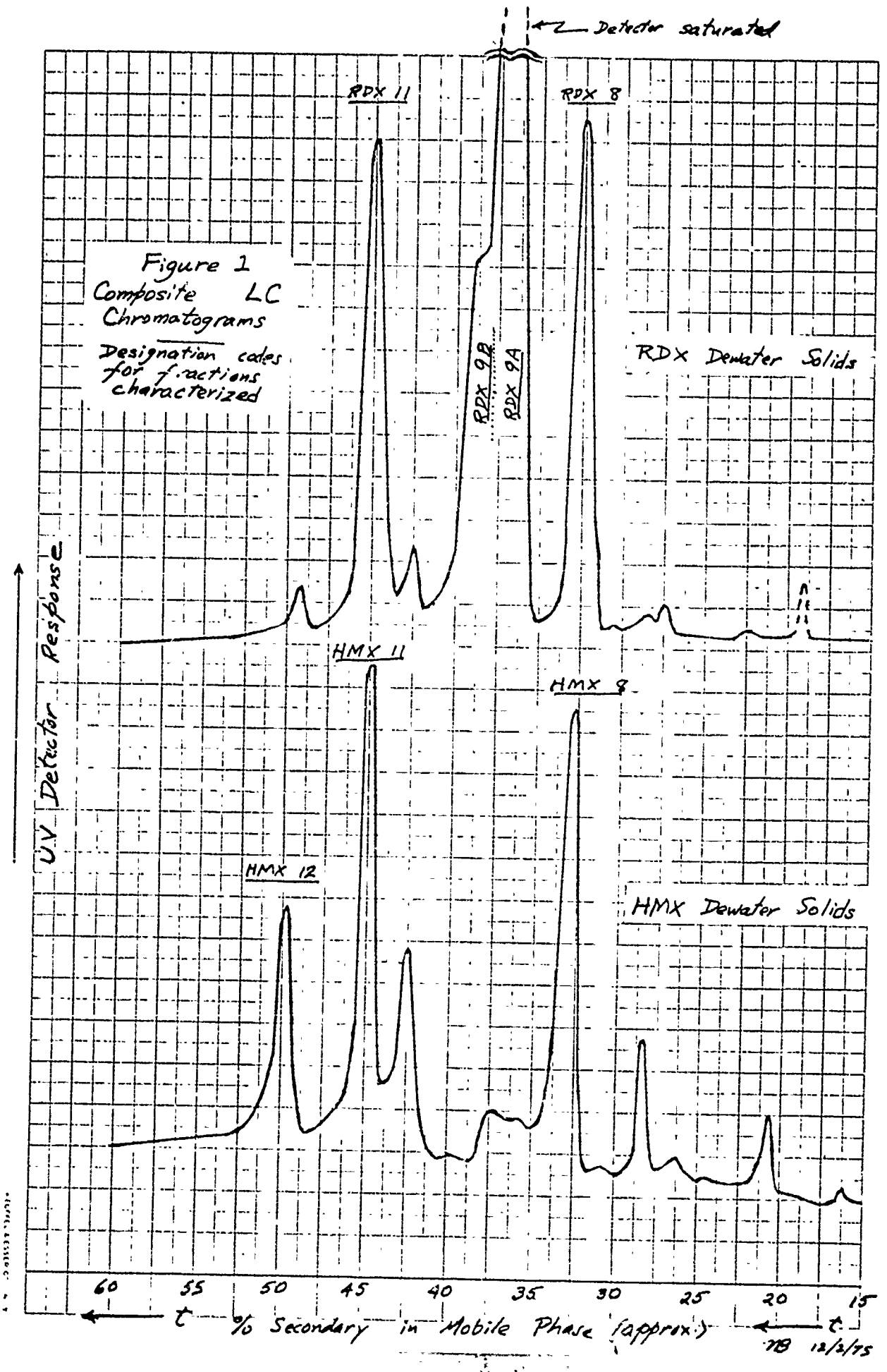


Figure 1
Composite LC Chromatograms

Designation codes for fractions characterized

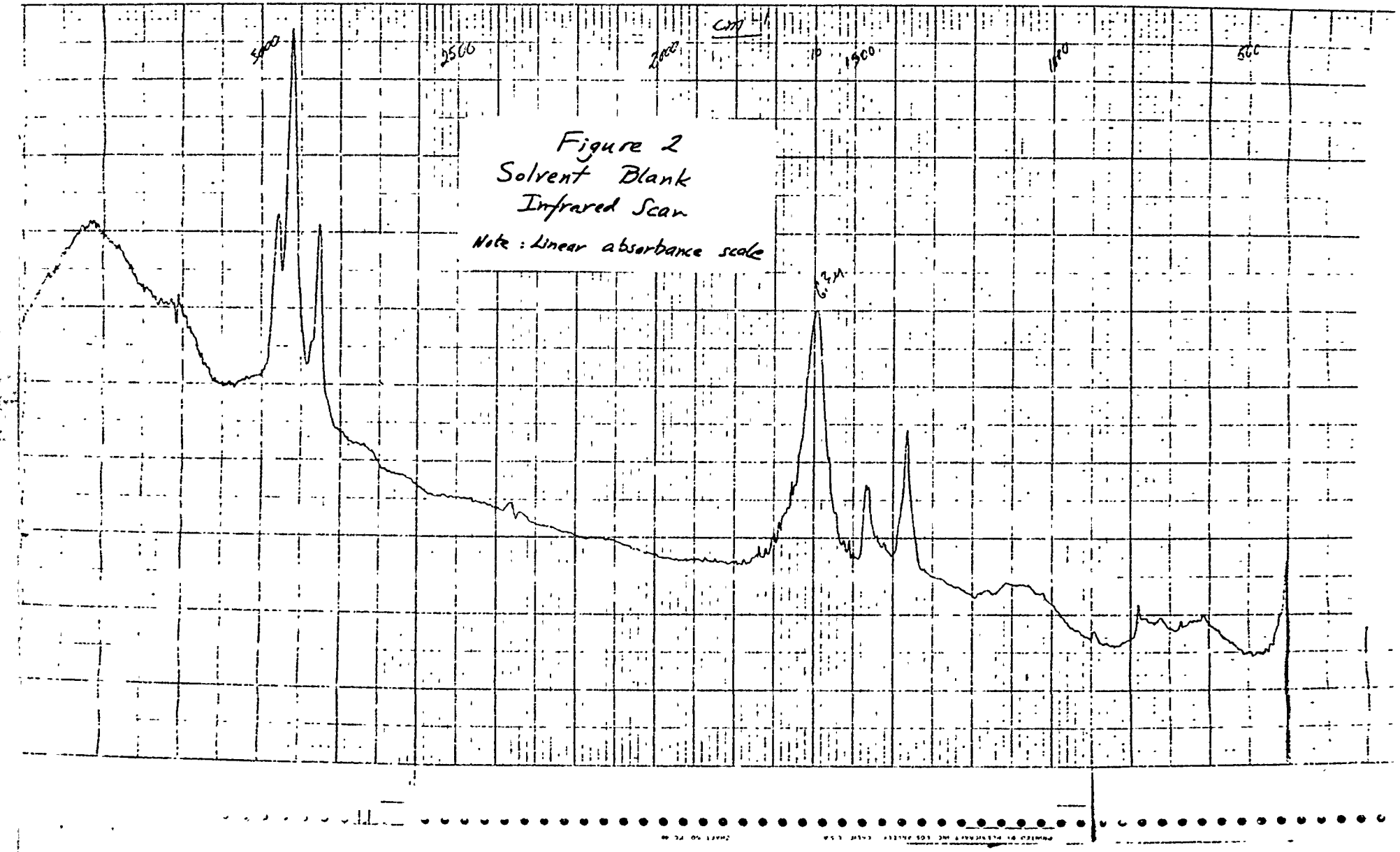


Figure 2
Solvent Blank
Infrared Scan

Note: Linear absorbance scale

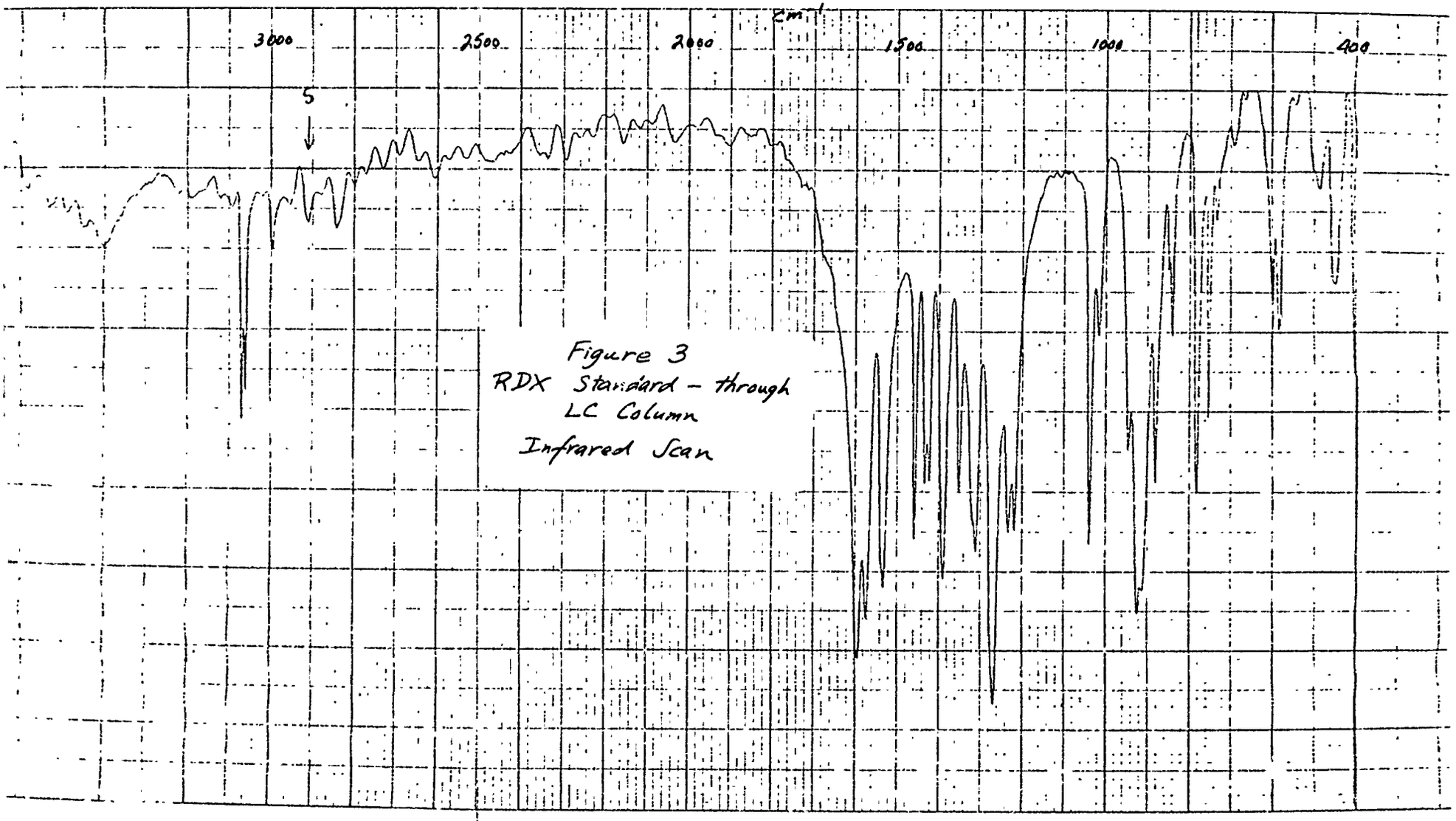


Figure 3
RDX Standard – through
LC Column
Infrared Scan

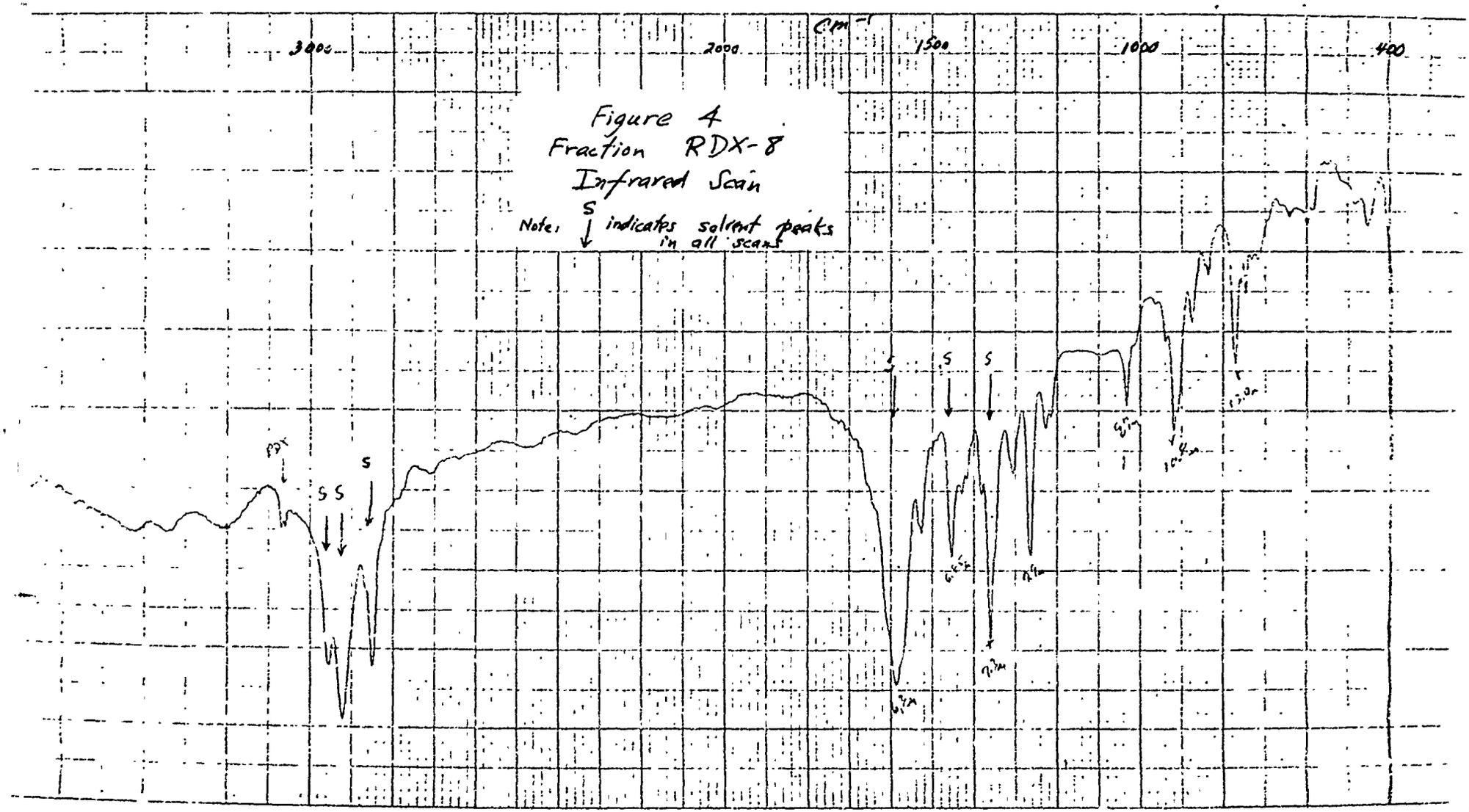


Figure 4
Fraction RDX-8
Infrared Scan

Note: S ↓ indicates solvent peaks in all scans

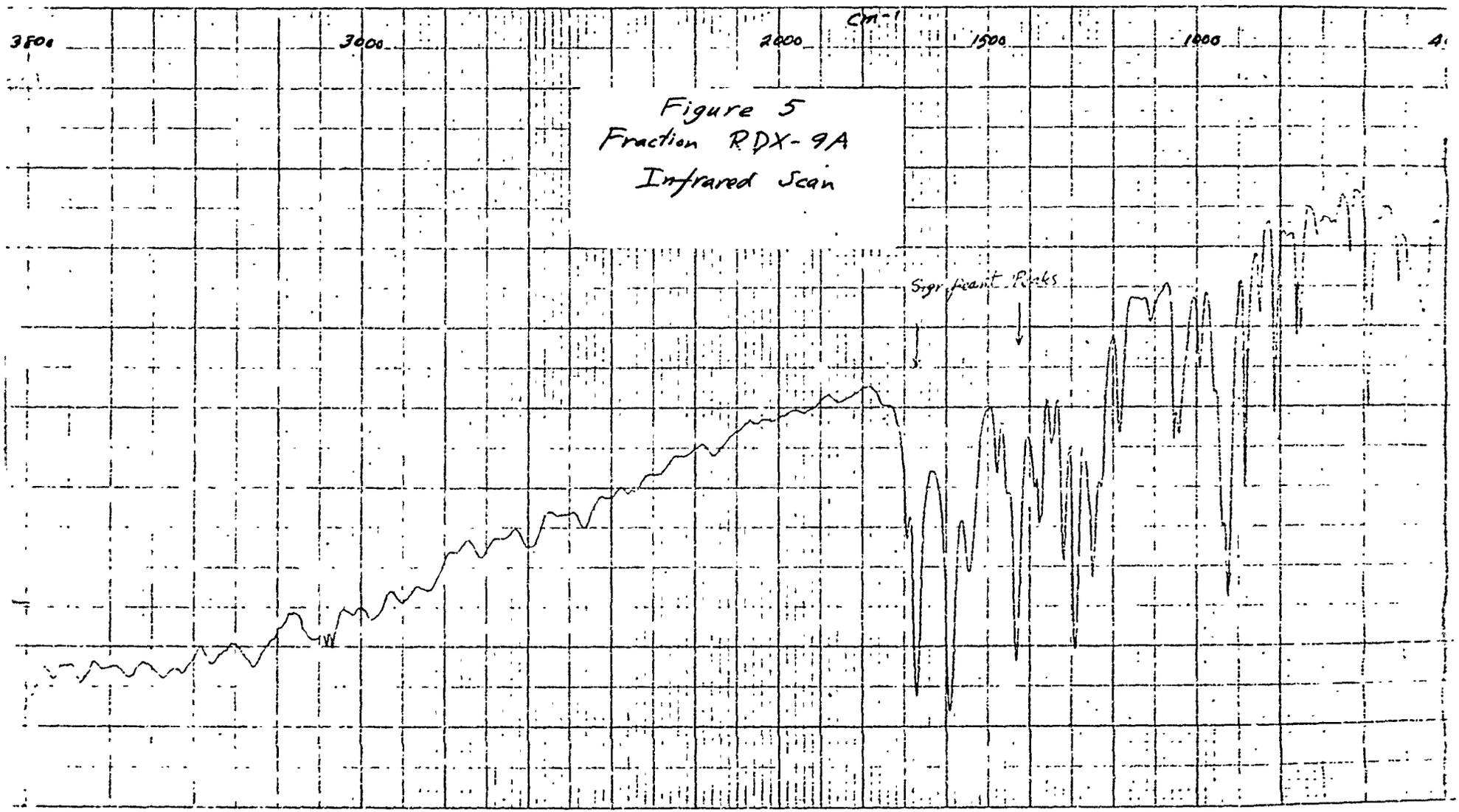


Figure 5
Fraction RDX-9A
Infrared Scan

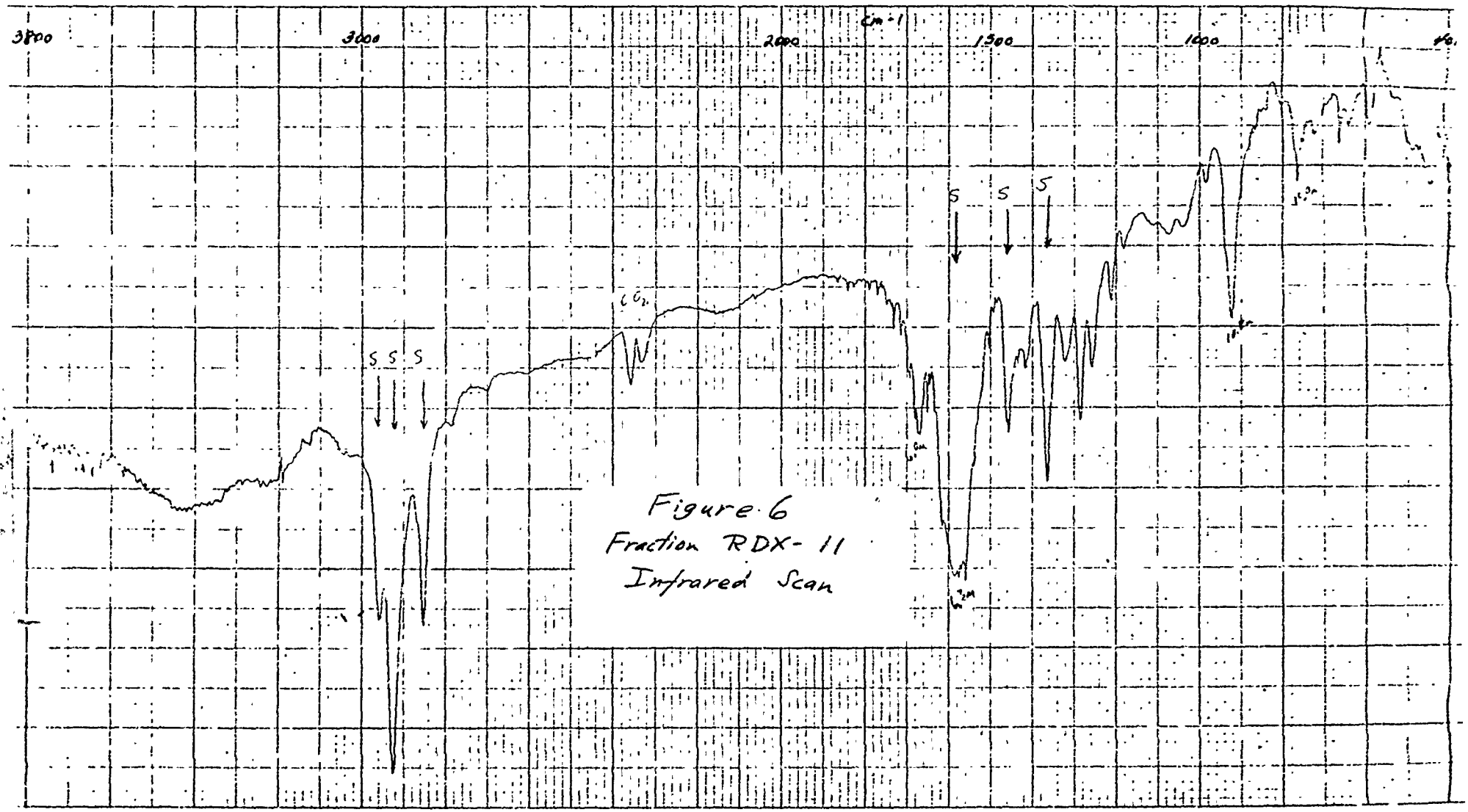


Figure 6
Fraction RDX-11
Infrared Scan

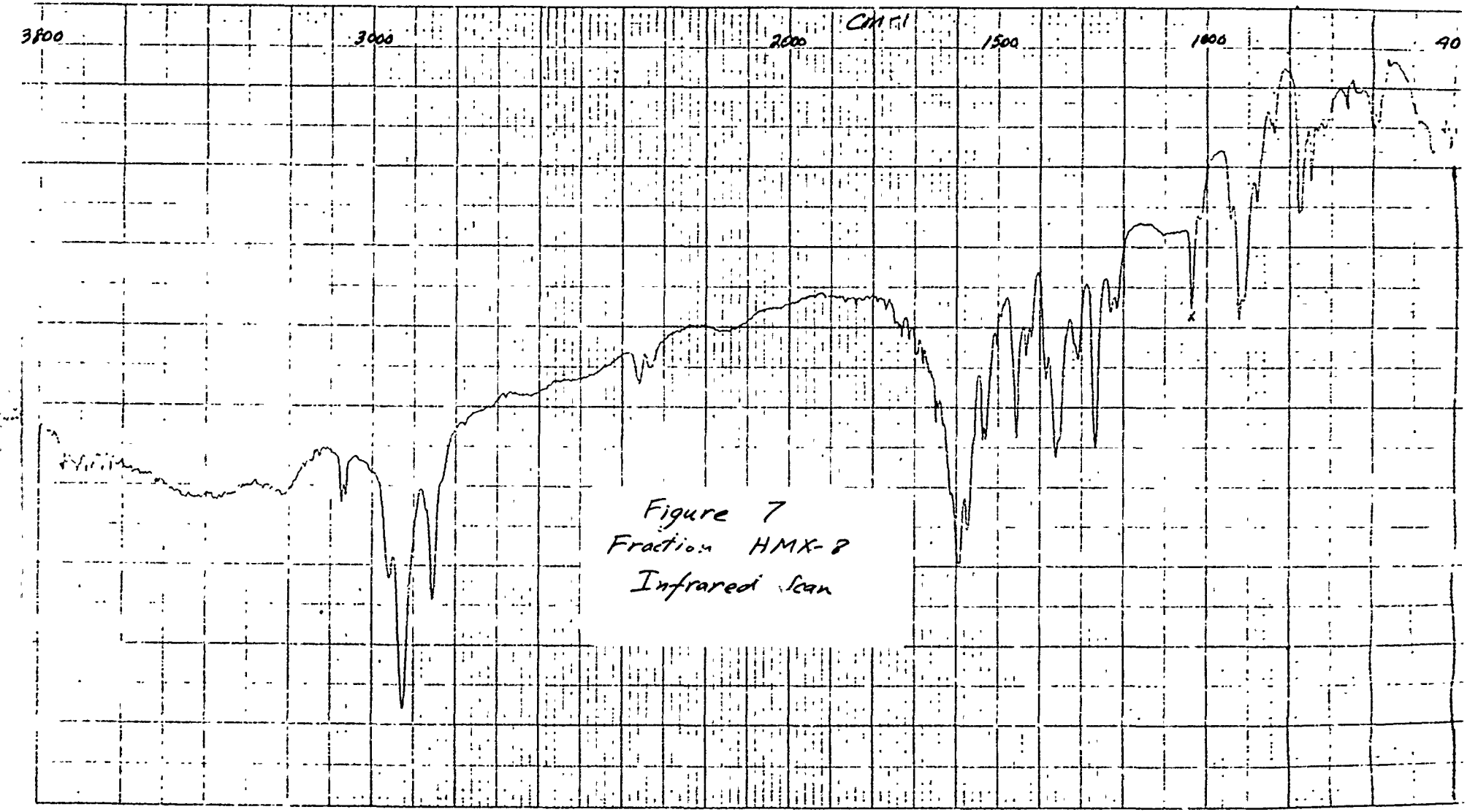


Figure 7
Fraction HMX-8
Infrared Scan

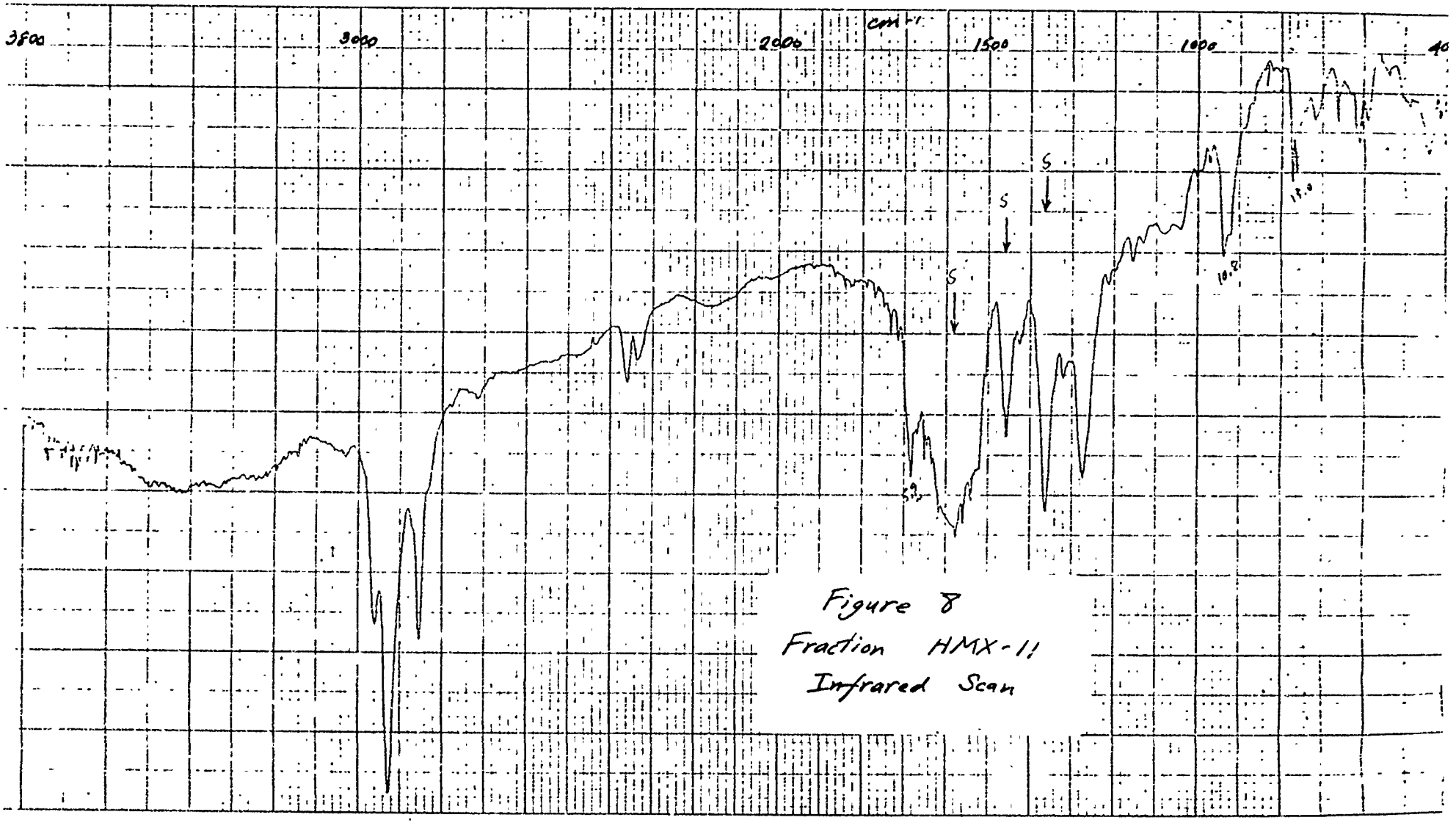


Figure 8
Fraction HMX-11
Infrared Scan

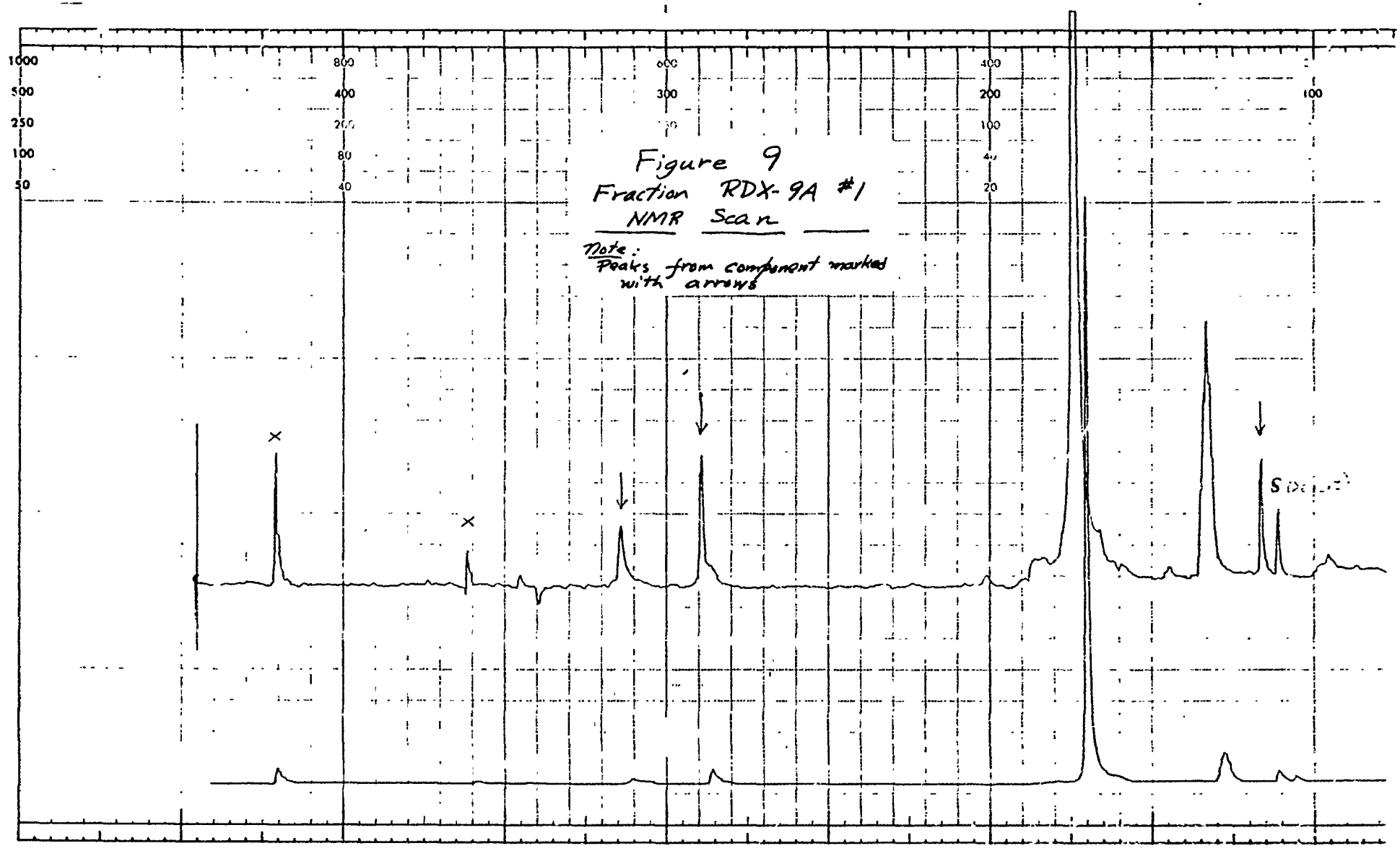
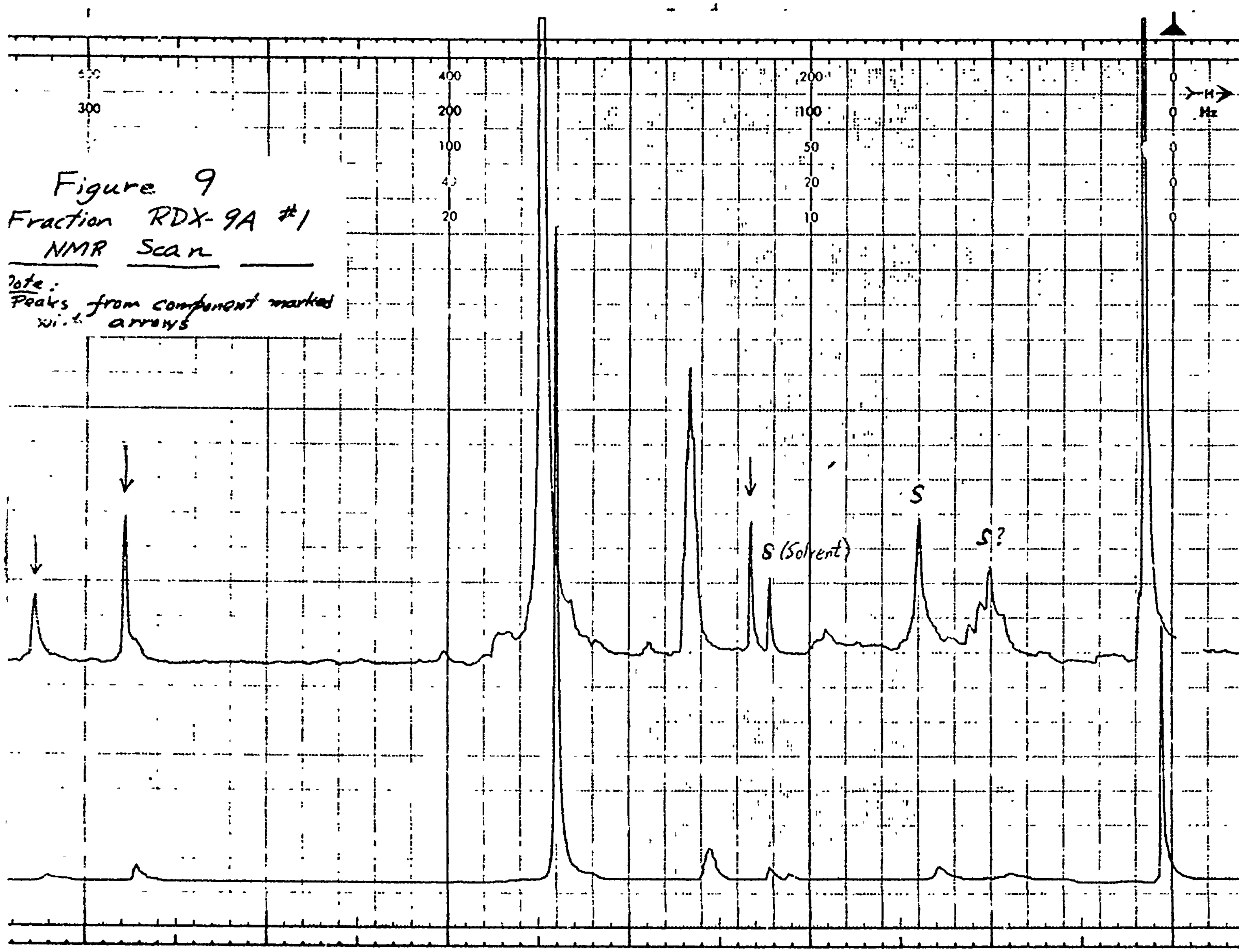

1000
500
250
100
50
800
400
200
80
40
600
300
100
400
200
100
40
20
Figure 9
Fraction RDX-9A #1
NMR Scan
Note:
Peaks from component marked
with arrows

Figure 9
Fraction RDX-9A #1
NMR Scan

Note:
Peaks from component marked with arrows



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4	445	0.[illegible]	0.[illegible]
5	676	0.[illegible]	4.[illegible]
6	756	0.043	0.[illegible]
7	791	0.[illegible]	0.373
8	80?	0.01?	0.[illegible]
9	864	0.0[illegible]	0.1[illegible]
10	902	0.013	0.17?
11	927	0.395	0.047
12	1008	0.322	1.249

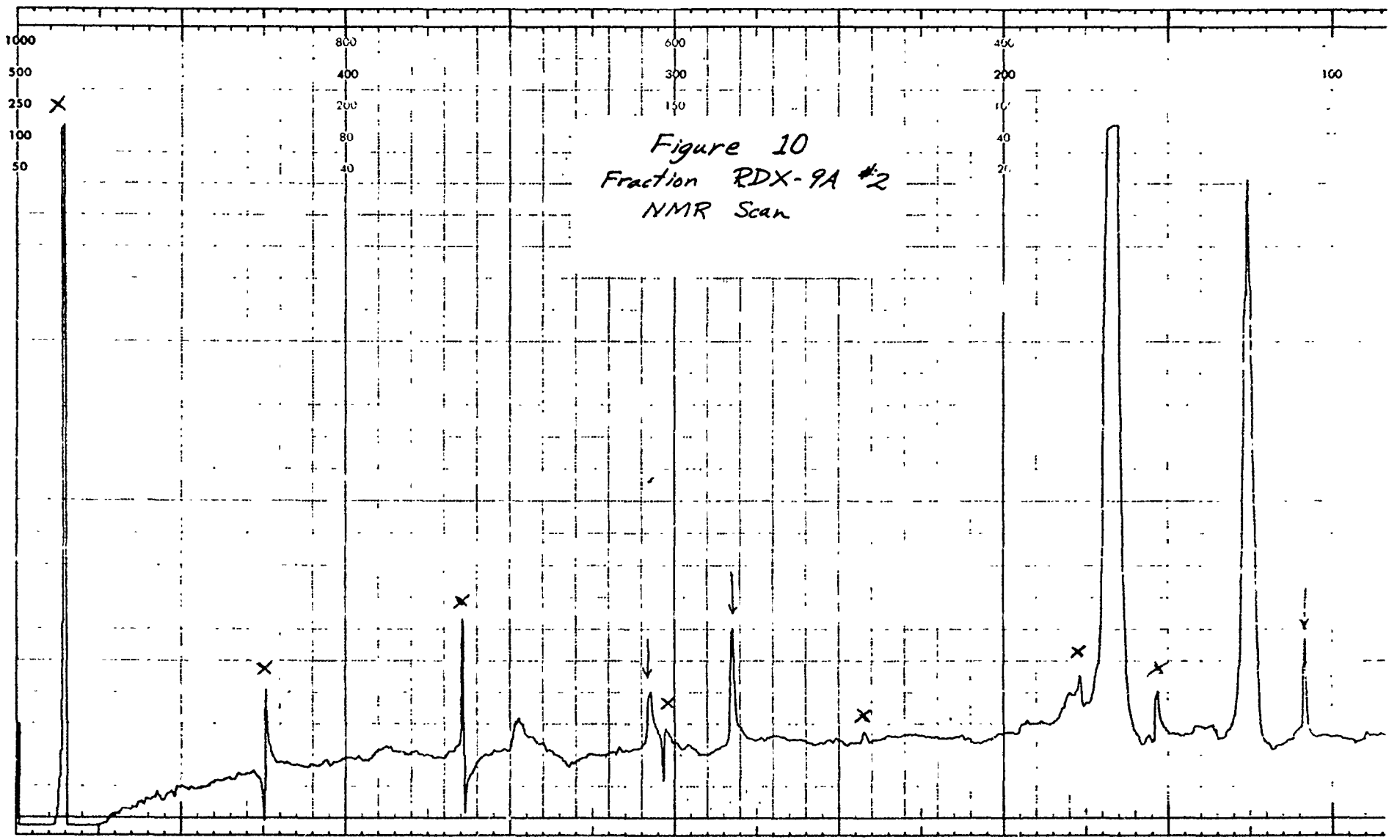

Figure 10
Fraction RDX-9A #2
NMR Scan

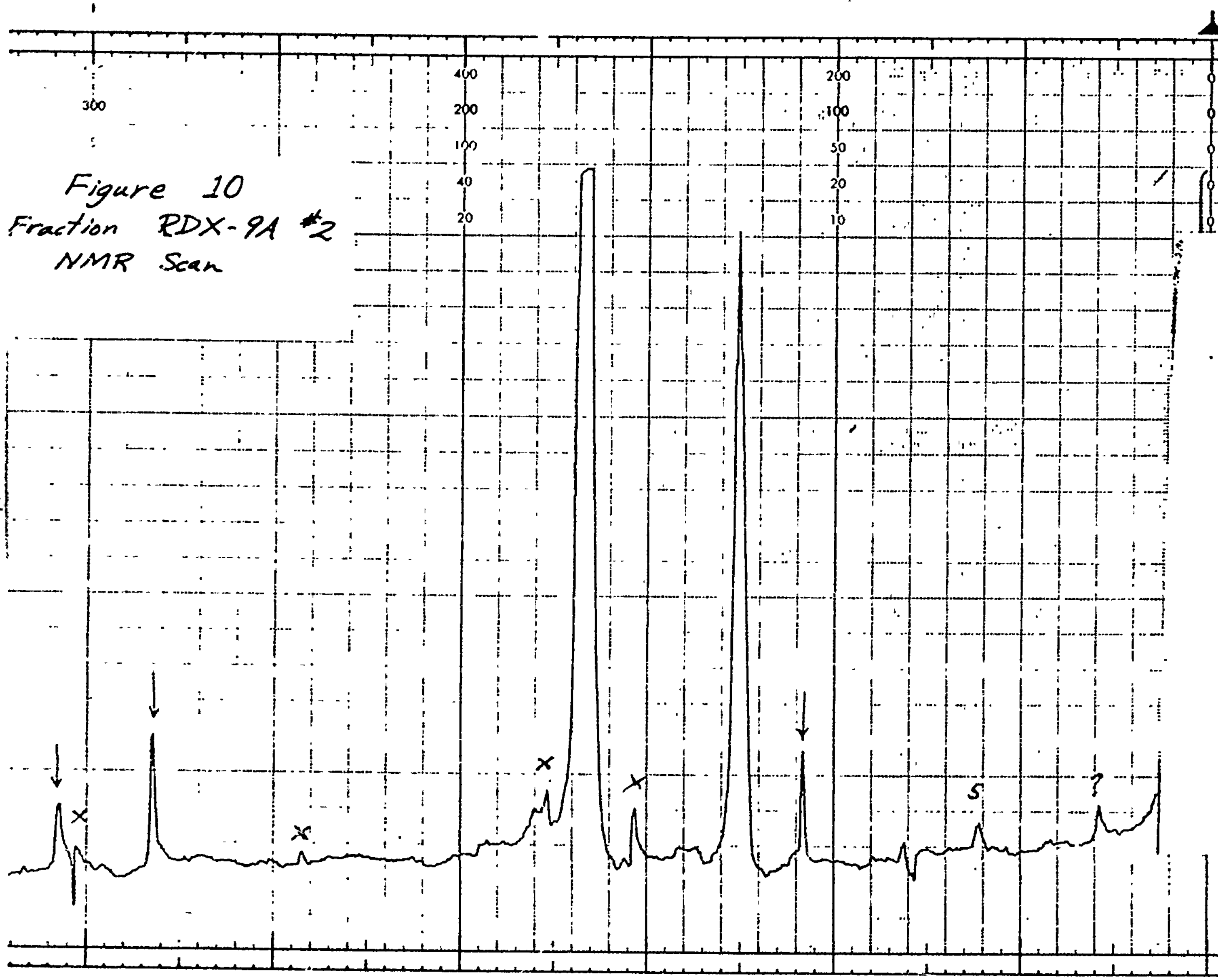

Figure 10
Fraction RDX-9A #2
NMR Scan

HA-100 SPECTRUM

100 MHz NMR
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OPERATOR: RSI DATE 10-8-75
SAMPLE: RDX-9A #2

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TYPE 1

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NSCANS= 500
NSCALE= 0
PKLOC = 99

RDX 9A FID

DO YOU WISH THIS FILE READ? (Y OR N) Y

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FLS=1 10
CIP
PLA
PPK
1
MAXIMUM VALUE = 0.047
MINIMUM VALUE = -0.012
SCALINGS = 7
PP

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3	299	0.012	0.016	[illegible].266
4	411	0.0[illegible]	0.015	4.102
5	463	[illegible]	0.0[illegible]	[illegible]
6	657	0.031	0.0[illegible]	3.671
7	693	0.814	1.239	[illegible].310
8	717	0.002	[illegible].014	[illegible].036
9	774	0.044	[illegible].864	[illegible]
10	807	0.037	[illegible].025	[illegible].135
11	901	0.002	0.013	1.030
12	965	0.033	0.043	0.595

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
BUFFALO, NEW YORK
No. VN 1006
(S-100A)

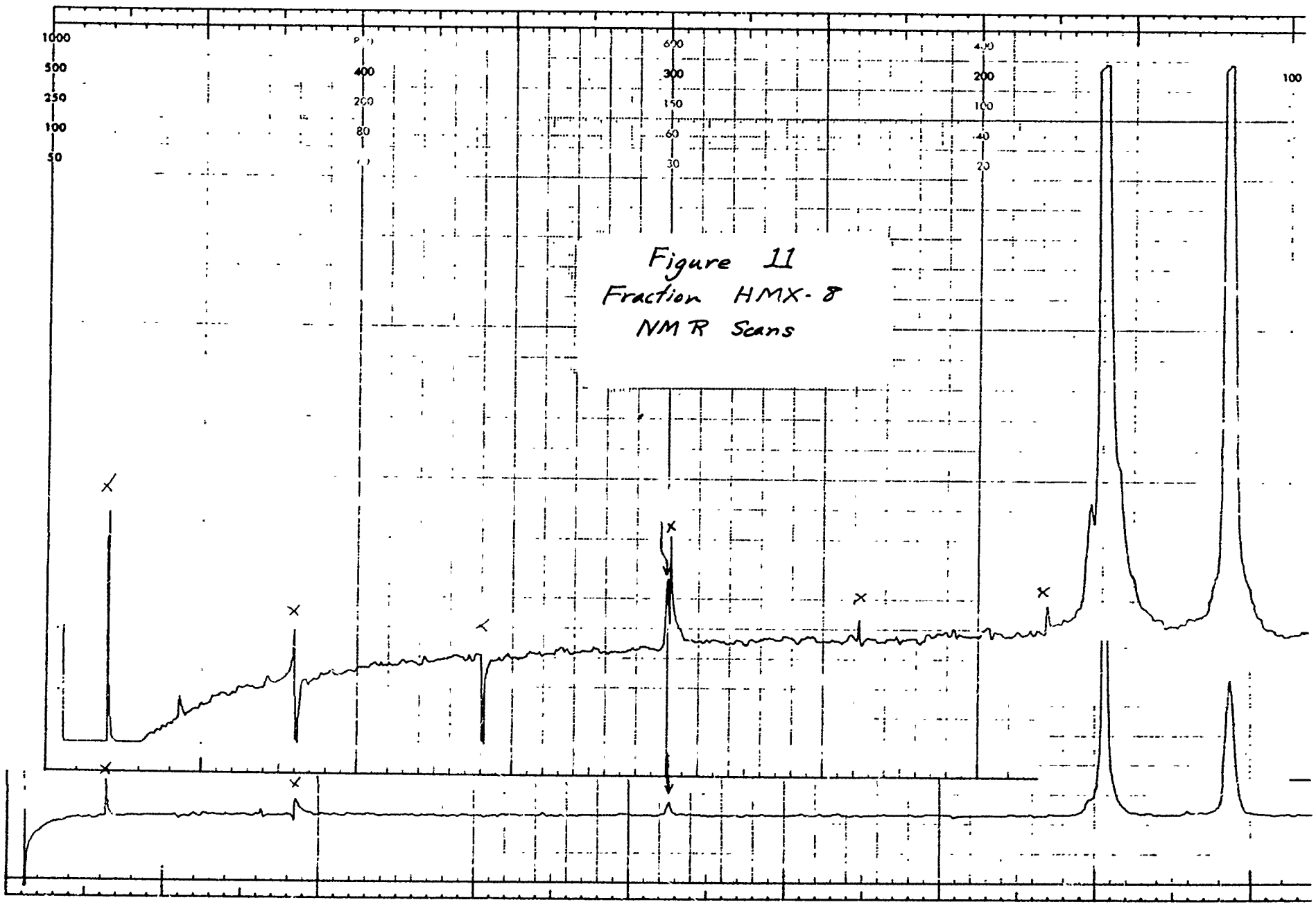

Figure 11
Fraction HMX-8
NMR Scans

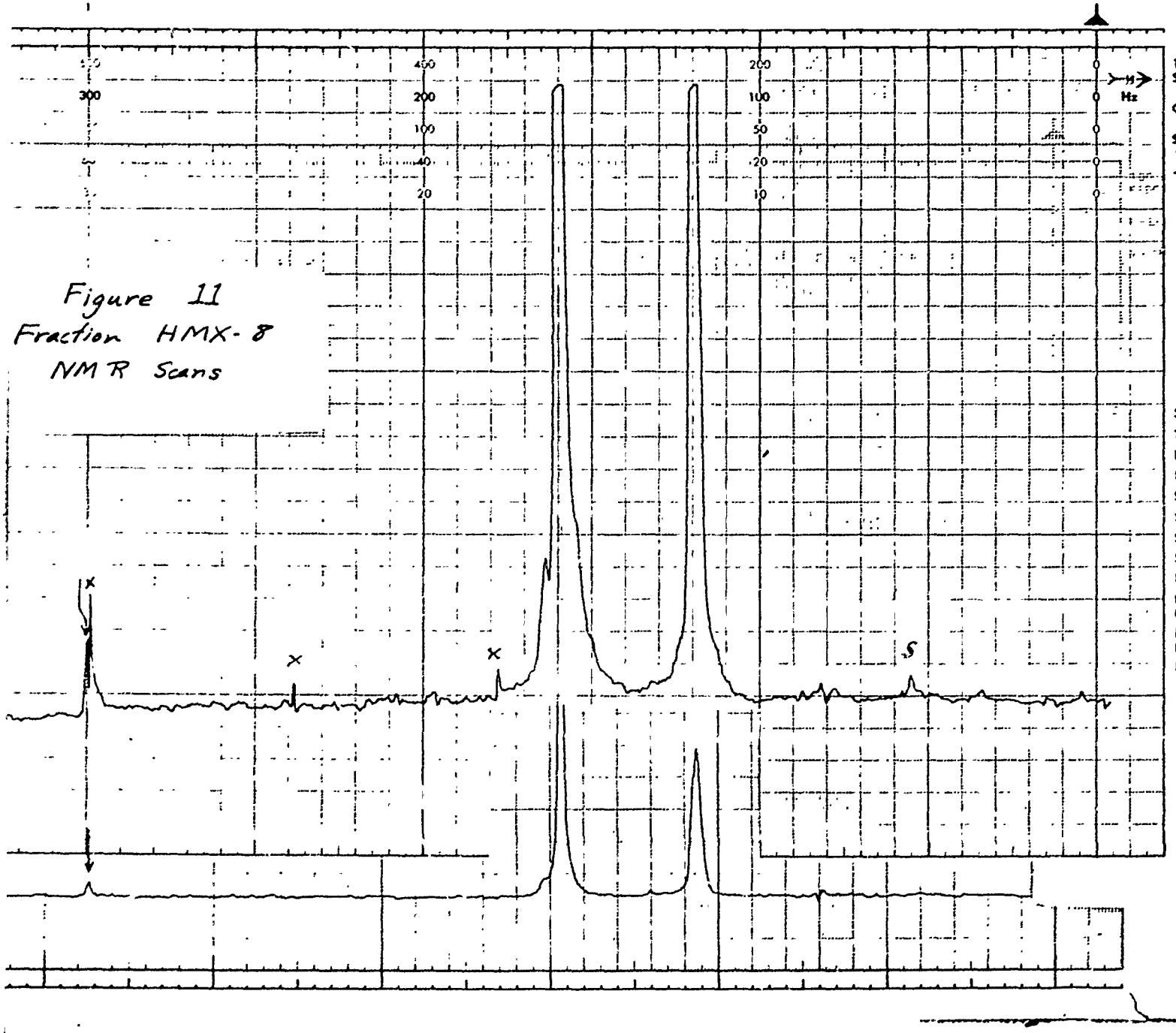

Figure 11
Fraction HMX-8
NMR Scans

HA-100 SPECTRUM

100 MHz NMR
SPECTRUM NO.

OPERATOR: RSI DATE 10-8-75

SAMPLE: HMX-8

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IDYYYY=-3.0099 --05
PLA
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MINIMUM VALUE = -3.088.
SCALINGS = 7
99

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TEMPERATURE				°C
FREQ. RESPONSE				Hz
R.F. ATTENUATOR				db
SWEEP TIME				sec
SWEEP WIDTH				Hz
SWEEP OFFSET				Hz
SPECTRUM AMP.				
LOCK SIGNAL				
FIELD MILLIGAUSS (MAN. OSC. FREQ.)				m. gauss
FIELD MILLIGAUSS (SWEEP FREQ.)				m. gauss

FIELD SWEEP ☐ FREQ. SWEEP ☐

VARIAN
GRAPHIC CONTROLS CORPORATION
BUFFALO NEW YORK

No. VN 1006

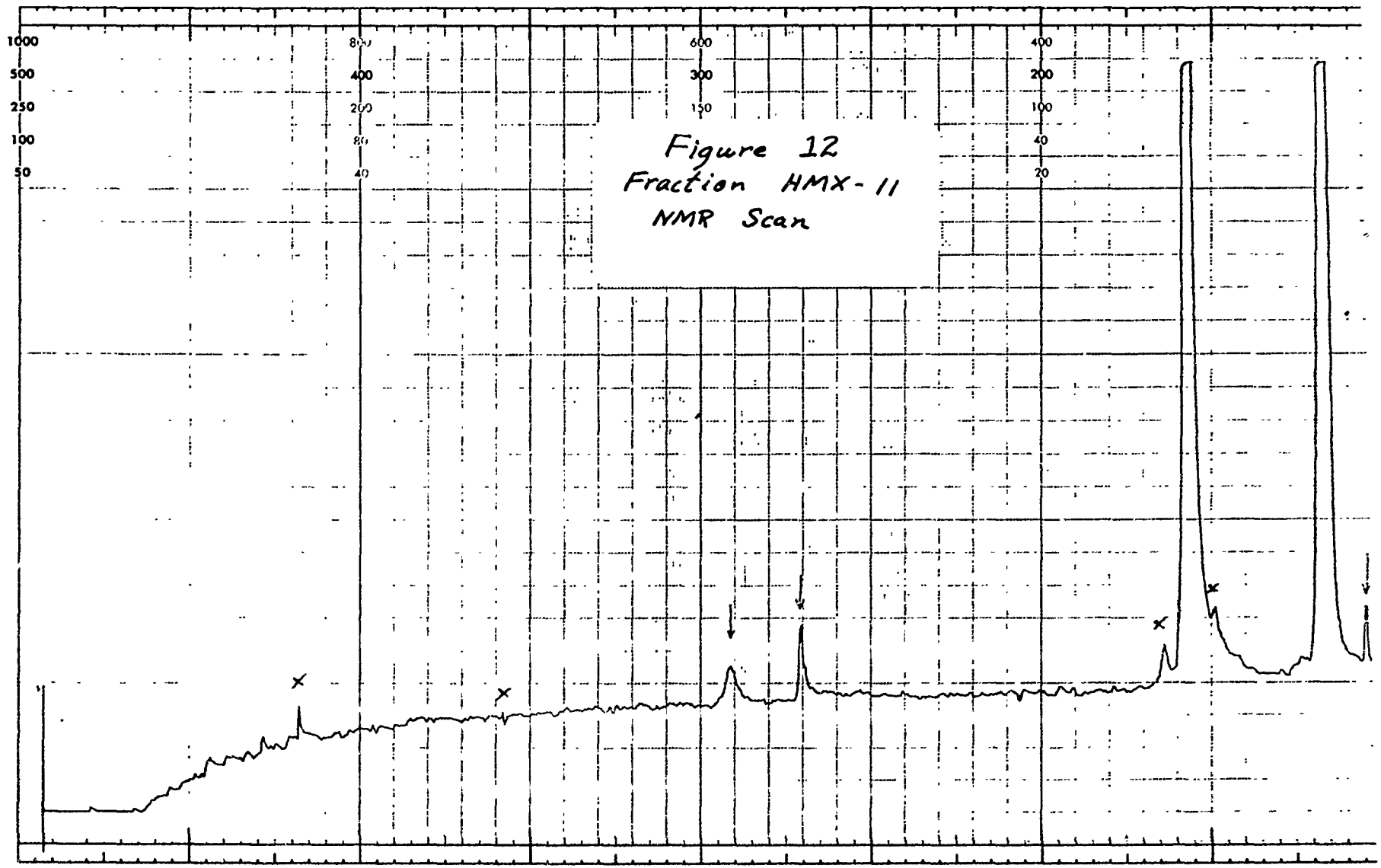

Figure 12
Fraction HMX-11
NMR Scan

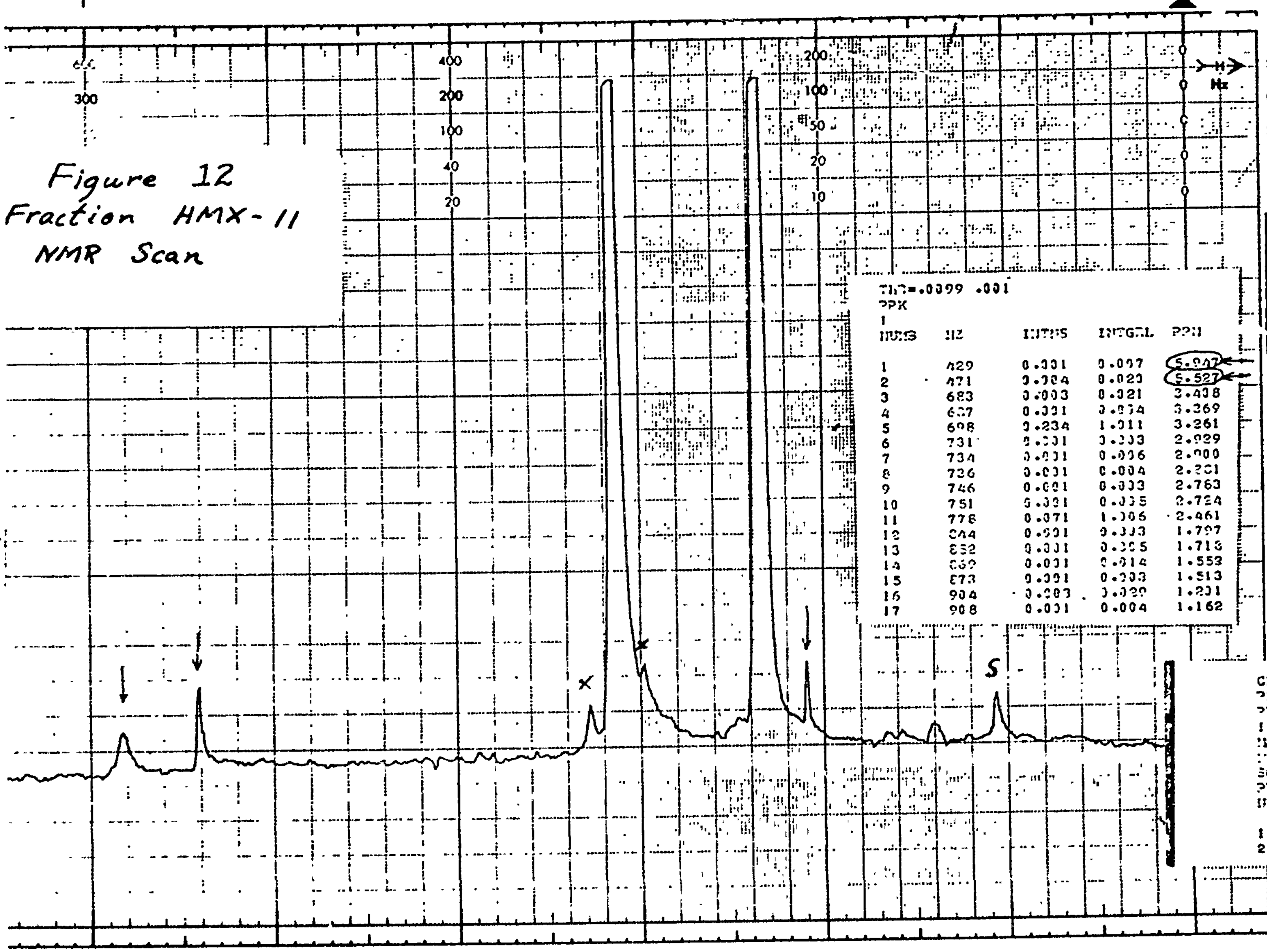

Figure 12
Fraction HMX-11
NMR Scan

HA-100 SPECTRUM

100 MHz NMR
SPECTRUM NO. ______

OPERATOR: RSS DATE 10-8-75

SAMPLE: HMX-11
9/22/72

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COL
1
RES = .976
BW = 2000
NPT = 4096
MEASUREMENT TIME = 1020 SEC
500

TYPE HEADER REMARKS.

HMX 11 FID

FILE NUMBER 6
TYPE 1

FILE SIZE = 4096
CYCLS = 0
NSCAN = 500
NSCAL = 2
NLOC = 99

HMX 11 FID

THR=.0099 .001
PPK
1

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2	471	0.004	0.020	5.527
3	683	0.003	0.021	3.408
4	687	0.001	0.034	3.369
5	698	0.234	1.011	3.261
6	731	0.001	0.003	2.929
7	734	0.001	0.006	2.900
8	736	0.001	0.004	2.881
9	746	0.001	0.003	2.763
10	751	0.001	0.005	2.724
11	778	0.071	1.006	2.461
12	844	0.001	0.003	1.797
13	852	0.001	0.005	1.718
14	869	0.001	0.014	1.553
15	873	0.001	0.003	1.513
16	904	0.003	0.020	1.201
17	908	0.001	0.004	1.162

CMP
PLA
PPK
1
MAXIMUM VALUE = 0.339
MINIMUM VALUE = -0.008
SCALINGS = 7
PP

NUMB	HZ	INTNS	INTGRL	PPM
1	598	0.234	0.516	3.261
2	778	0.071	0.334	2.461

NO. VN 1006
(S-100A)

APPENDIX C

Data Package Forwarded
to
Midwest Research Institute,
December, 1976

Figures C-1A to C-11A

HIGH PERFORMANCE LIQUID CHROMATOGRAMS
OF REFERENCE COMPOUNDS SHIPPED TO
MIDWEST RESEARCH IN DECEMBER, 1976

HPLC Conditions

Instrument:	Waters Associates Model 202 HPLC
Column:	Stainless Steel, 0.91 m x 6.3 mm (12 in. x 0.25 in.), Si60 LiChrosorb, 5μ MPS
Mobile Phase:	5% Methanol, 10% acetonitrile, 15% chloroform, 70% iso-octane
Flow Rate:	4.0 ml/min.
Pressure:	3000 psi
Detector:	UV at 254 nm
Injection Volume:	20 microliters

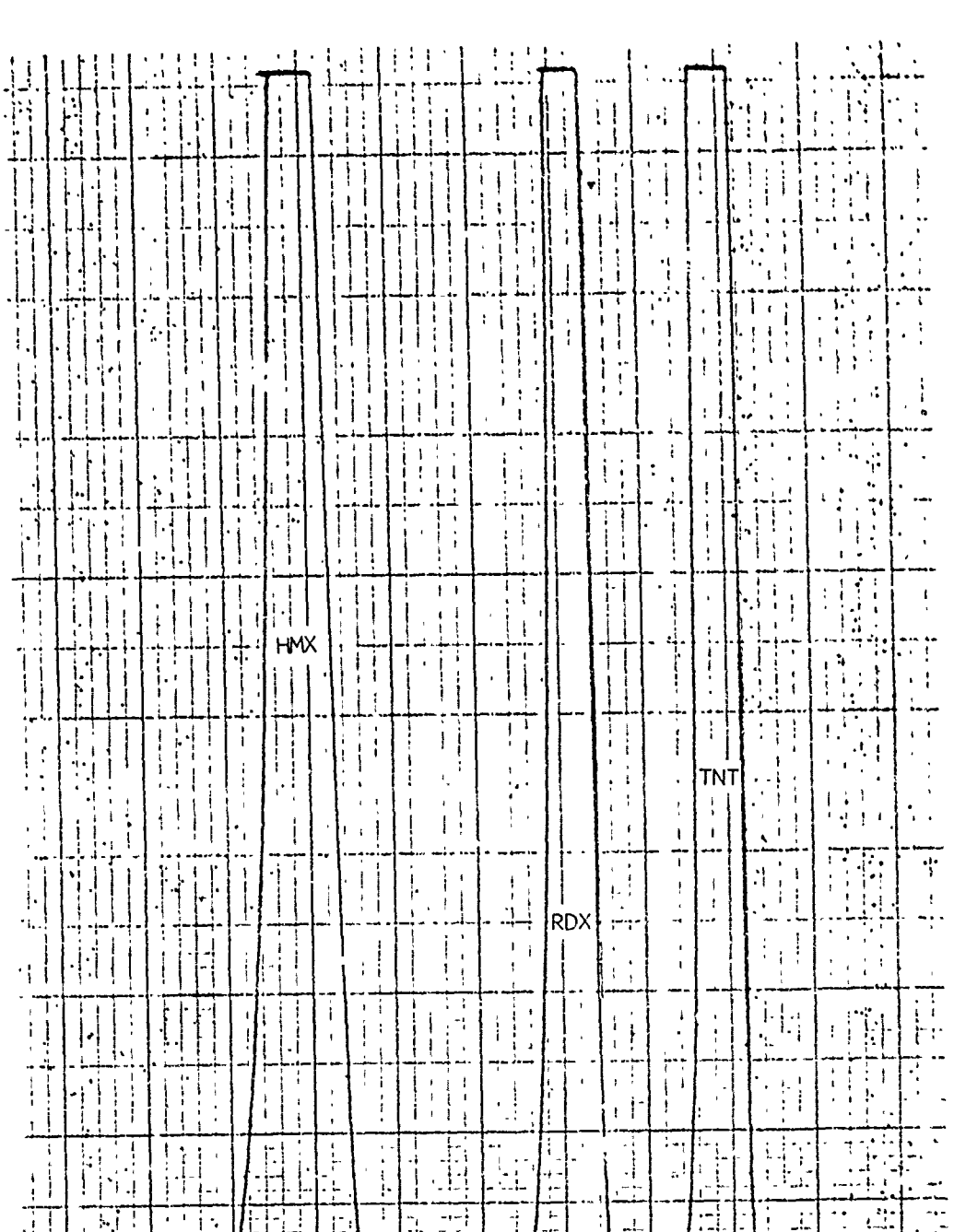


Figure C-1A. HPLC Chromatogram of Reference Compounds

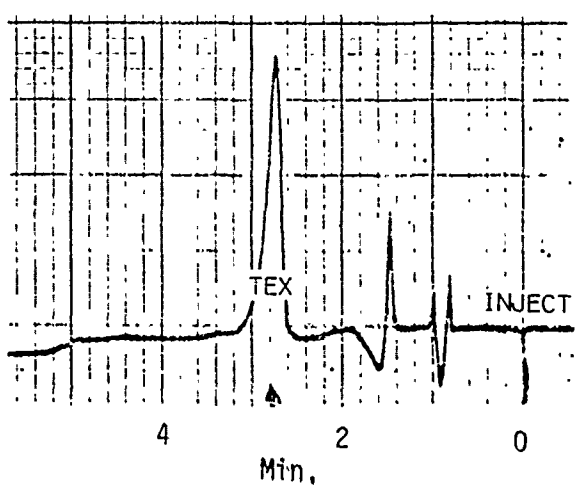


Figure C-2A. HPLC Chromatogram of Reference Compound

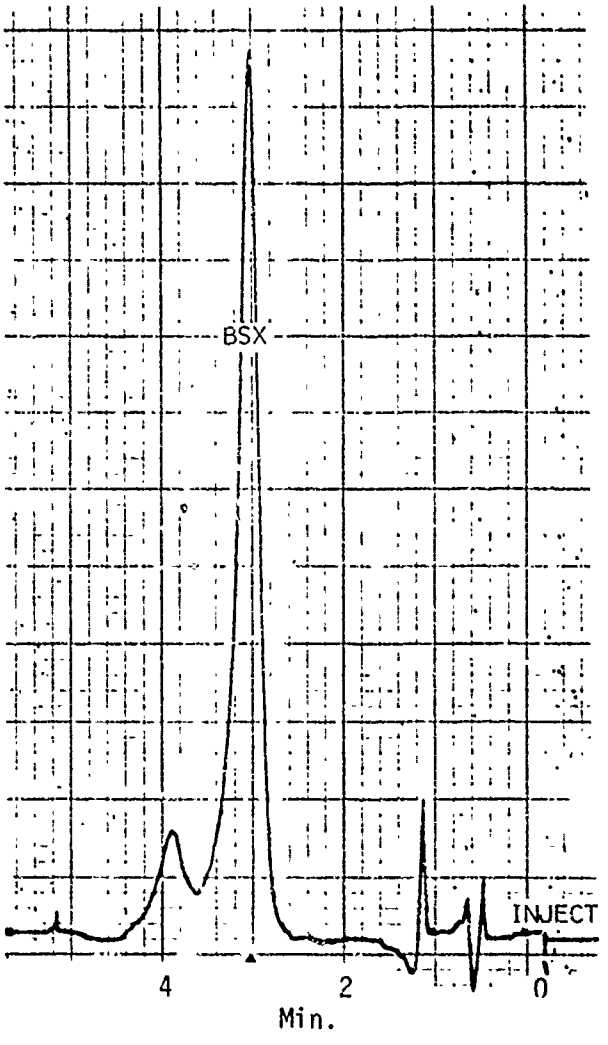


Figure C-3A. HPLC Chromatogram of Reference Compound

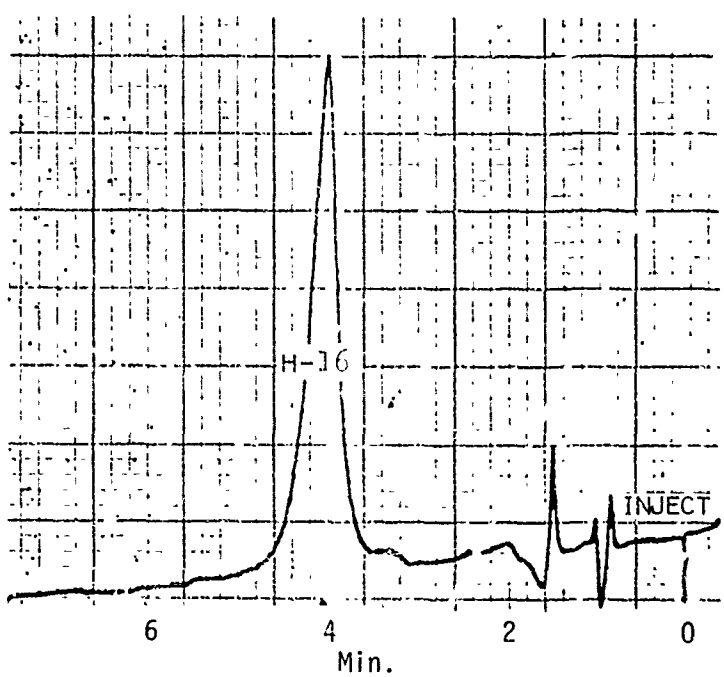


Figure C-4A. HPLC Chromatogram of Reference Compound

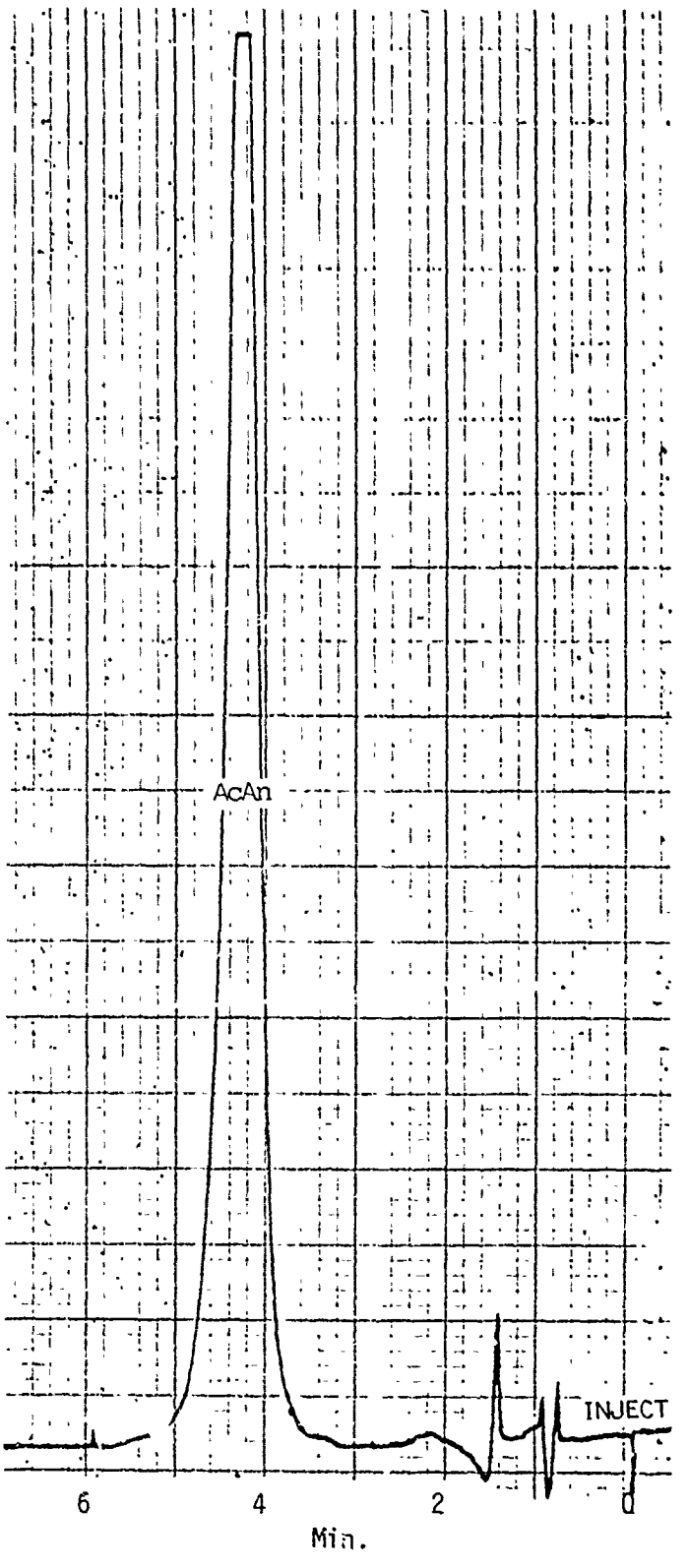


Figure C-5A. HPLC Chromatogram of Reference Compound

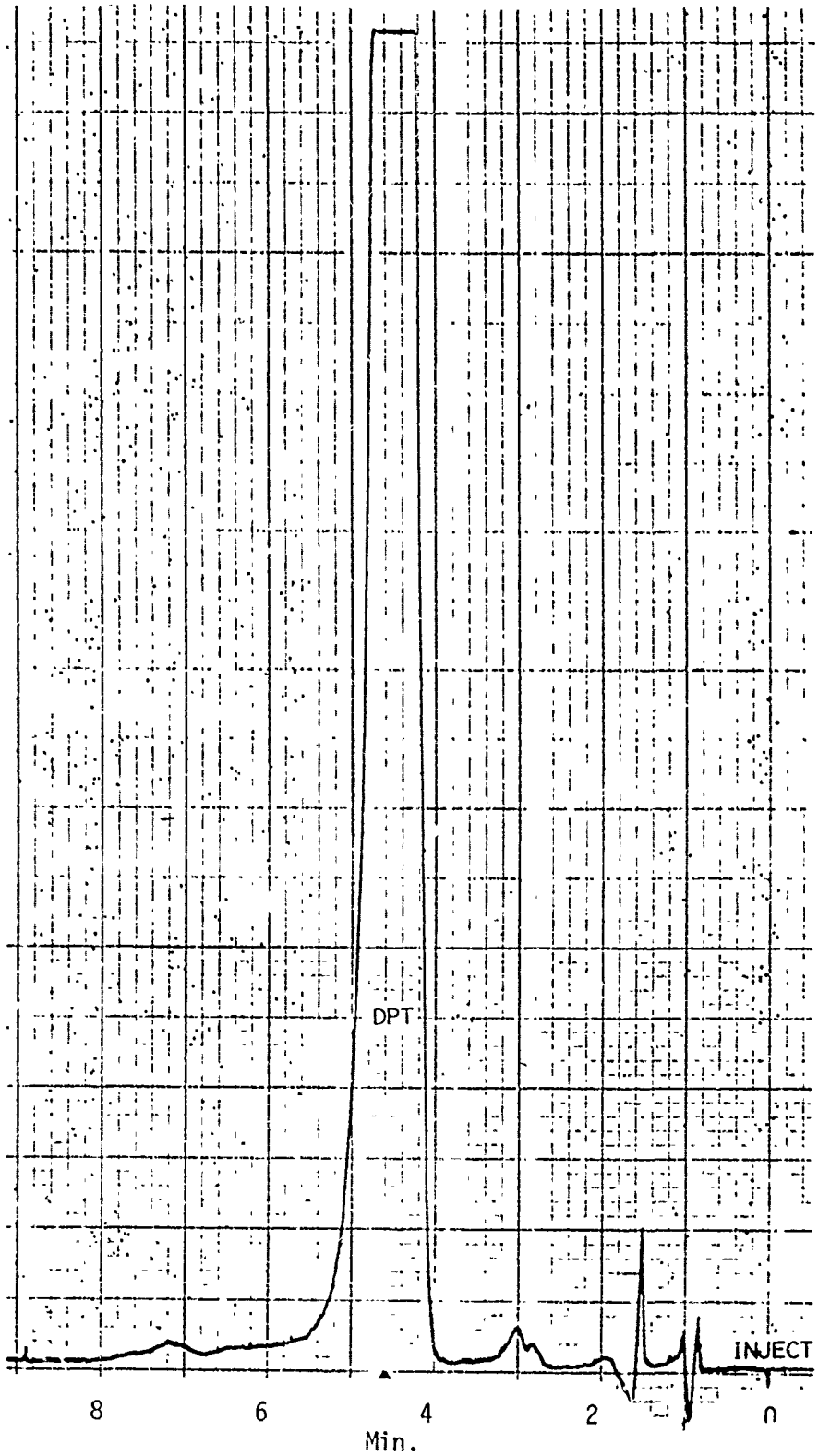


Figure C-6A. HPLC Chromatogram of Reference Compound

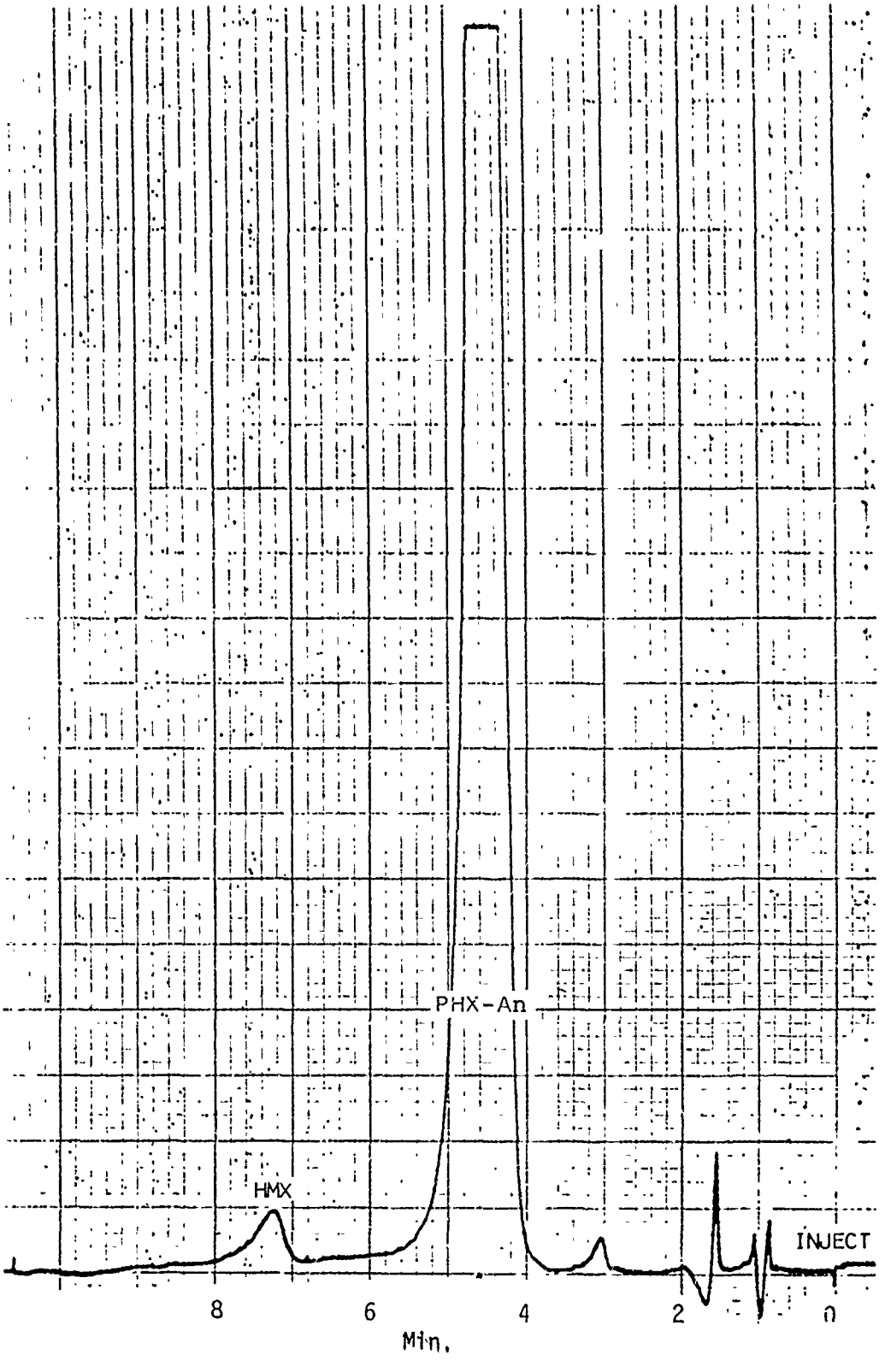


Figure C-7A. HPLC Chromatogram of Reference Compound

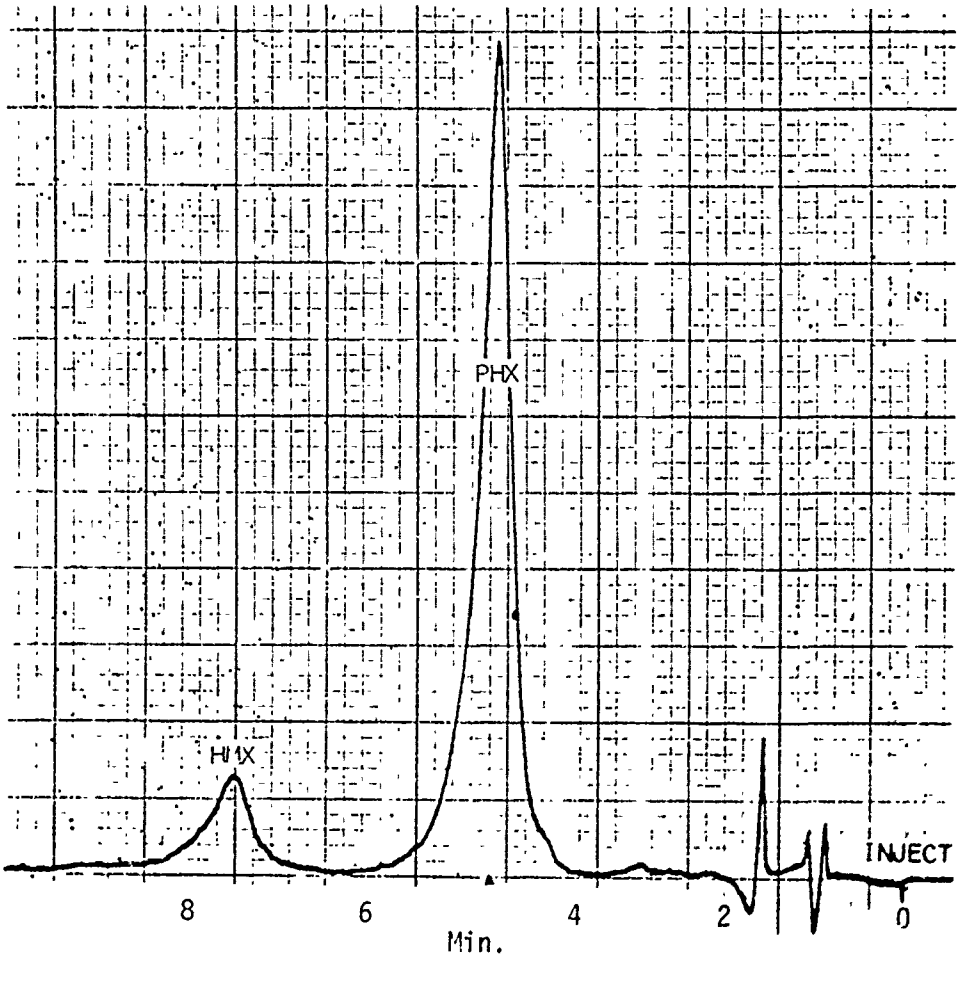


Figure C-8A. HPLC Chromatogram of Reference Compound

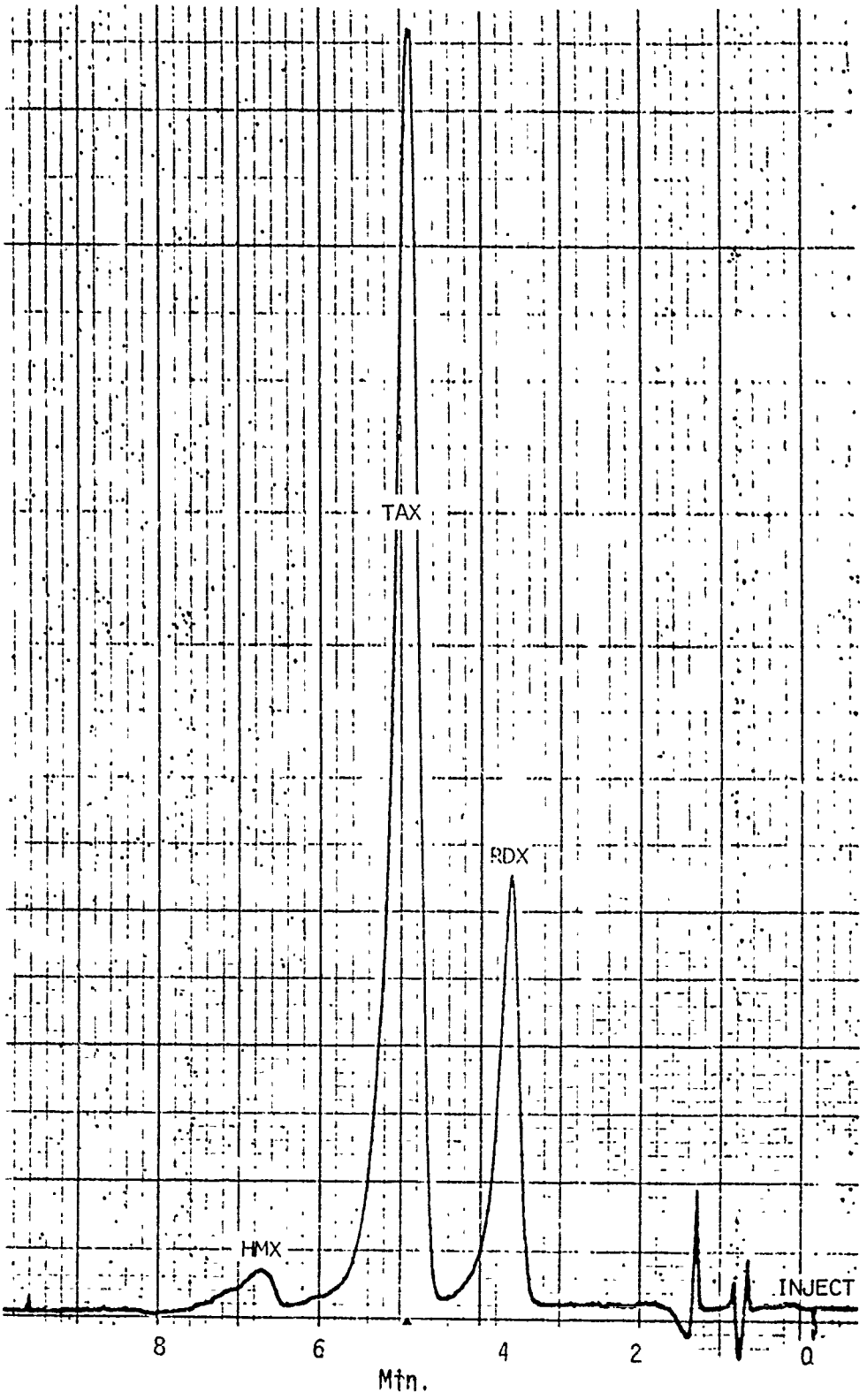


Figure C-9A. HPLC Chromatogram of Reference Compound

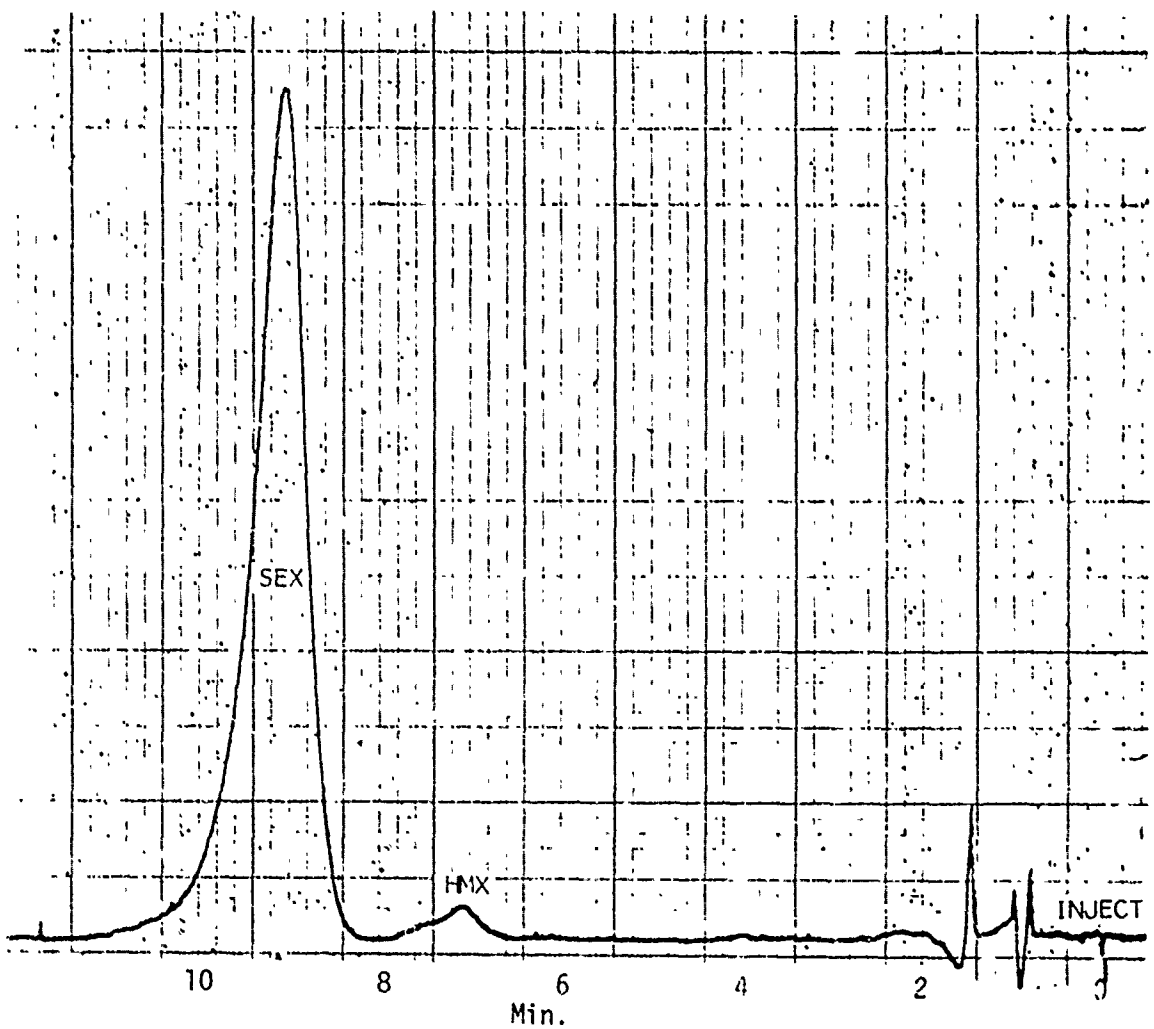


Figure C-10A. HPLC Chromatogram of Reference Compound

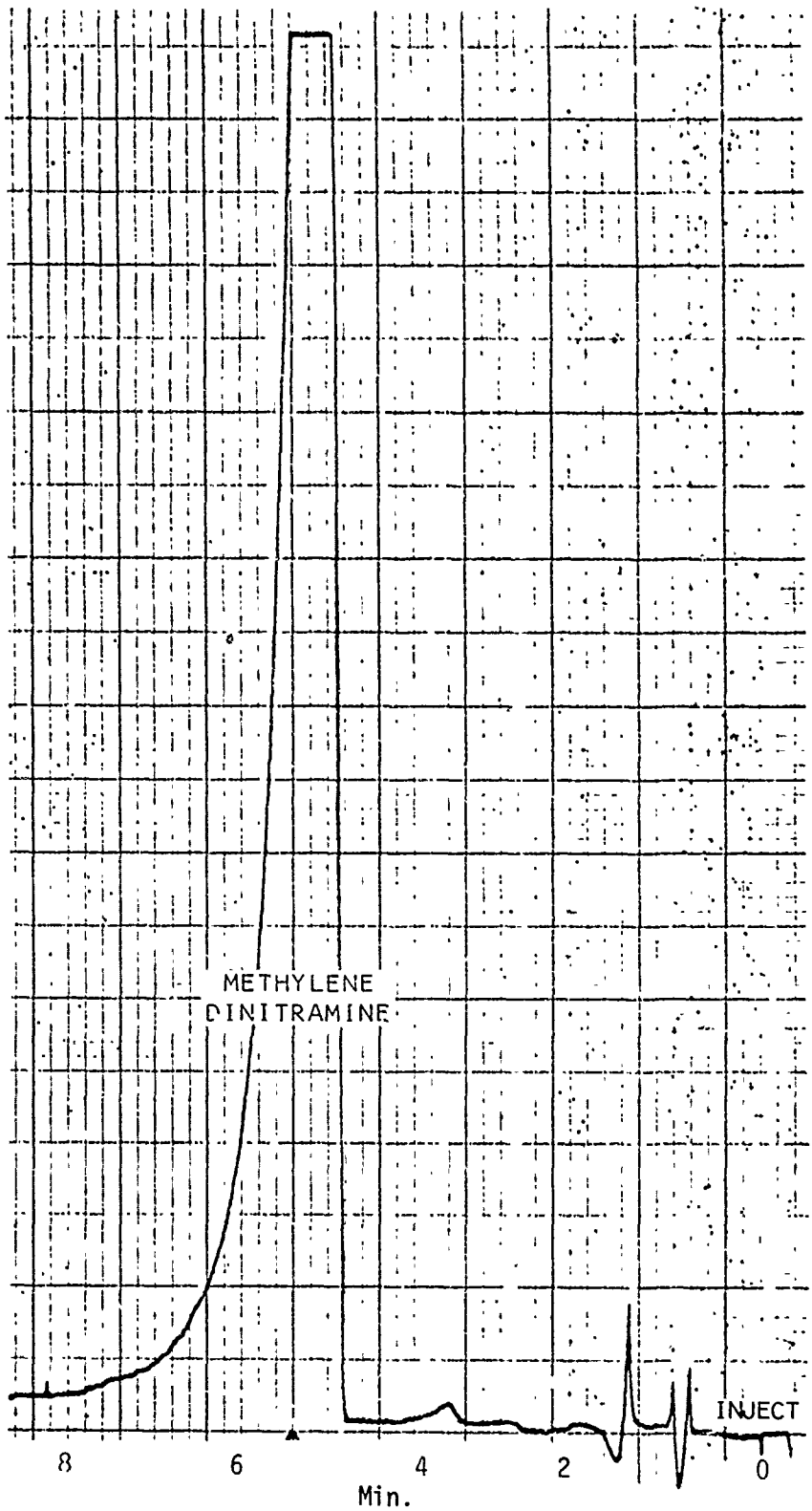


Figure C-11A. HPLC Chromatogram of Reference Compound

Figures C-1B to C-16B

HIGH PERFORMANCE LIQUID CHROMATOGRAMS OF INDIVIDUAL FRACTION ISOLATED FROM RDX DEWATER

Pages 91 to 107

DATE 11-1-76 OPERATOR W. Fortune CHROMAT. NO. _____
COL NO. 52 LENGTH 12" ID 1/4" CW packed with _____ PCT.
(PHASE) PAC on (SUPPORT) _____
MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN, 15% $CHCl_3$, 75% Hexane
TEMPS. (Reservoir) amb (Col.) amb (Det.) amb
PRESSURE 1000 psi FLOW RATE 2.0 ml/min.
DET. 254 nm VSENS. .05 CHART SPEED 1/2 in /min.
SAMPLE RDX dewater solid fraction #1
SAMPLE CONC. _____ INJ. AMT. 10 µl

TIME	AREA %	
28	64.442	1-
35	33.472	S
56	2.084	\
187	.000	S

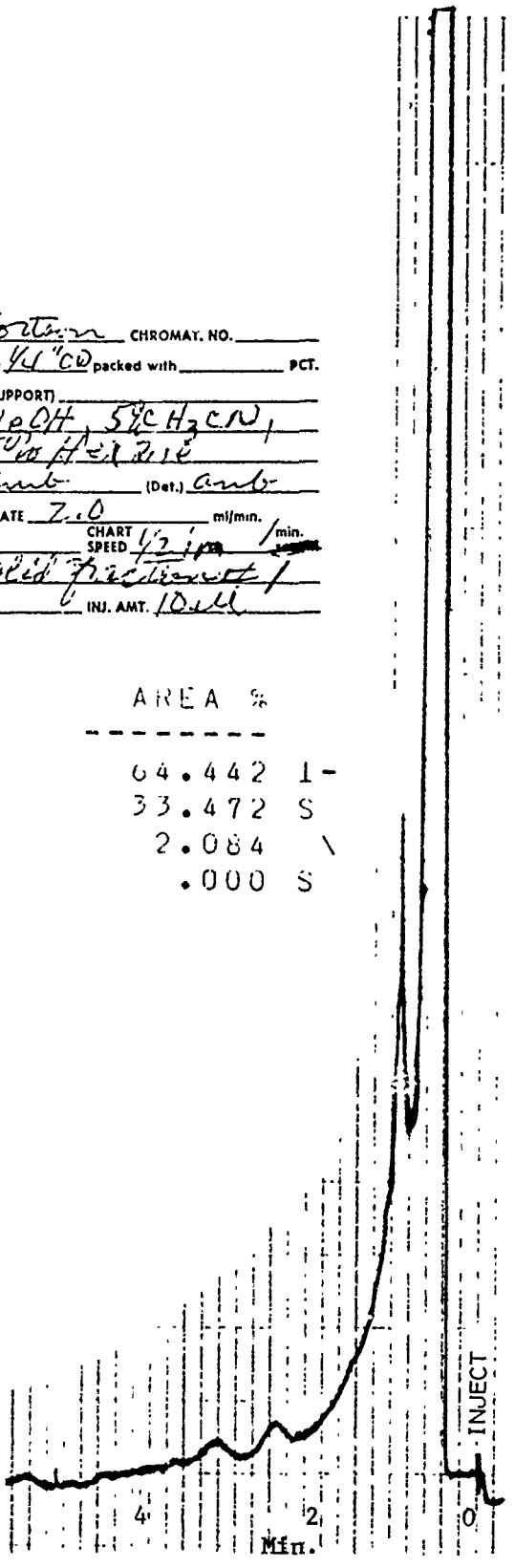


Figure C-1B. HPLC Chromatogram of RDX Dewater Fraction No. 1

DATE 11-1-76 OPERATOR H. Forston CHROMAT. NO. _____

COL. NO. 52 LENGTH 12" ID 1/4" O.D. packed with _____ PCT.

(PHASE) PAC on (SUPPORT) _____

MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN

15% $CHCl_3$, 75% Hexane

TEMPS. (Reservoir) Amb (Col.) Amb (Det.) Amb

PRESSURE 1000 FLOW RATE 2.00 ml/min.

DET. 254 nm SENS. .08 CHART SPEED 0.5 in ~~cm~~ min.

SAMPLE RDX dewater solid fraction #2.

SAMPLE CONC. _____ INJ. AMT. 10 ul

TIME	AREA %	
29	40.844	I -
35	56.104	S
56	3.050	\

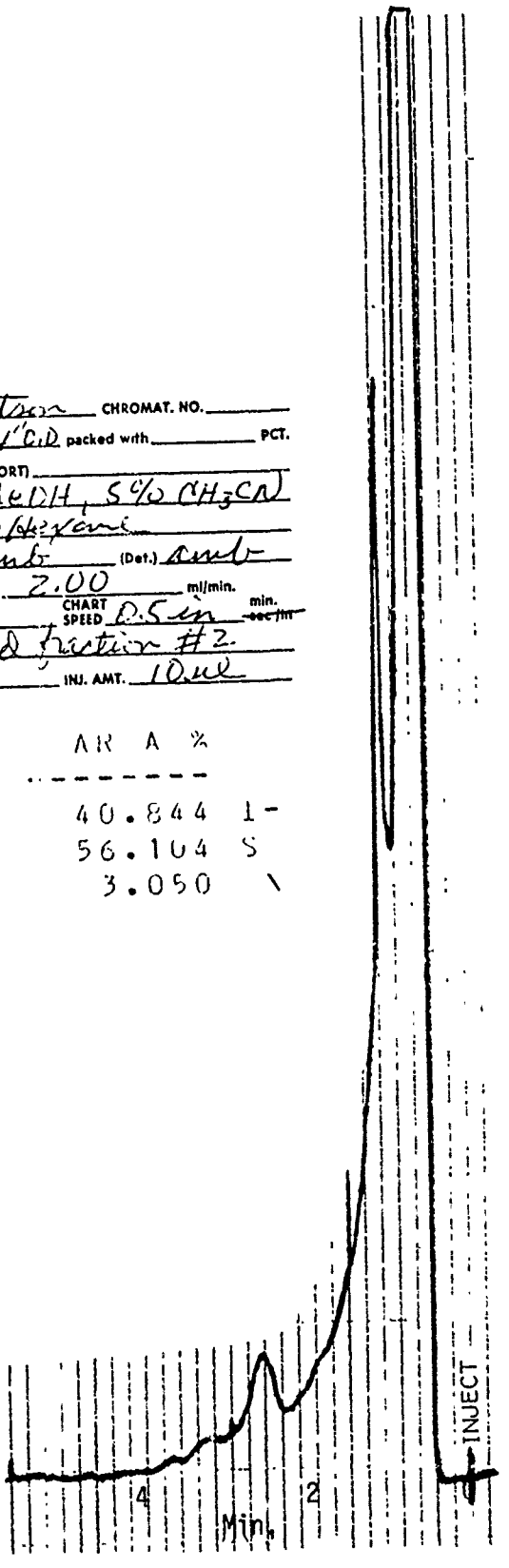


Figure C-2B. HPLC Chromatogram of RDX Dewater Fraction No. 2

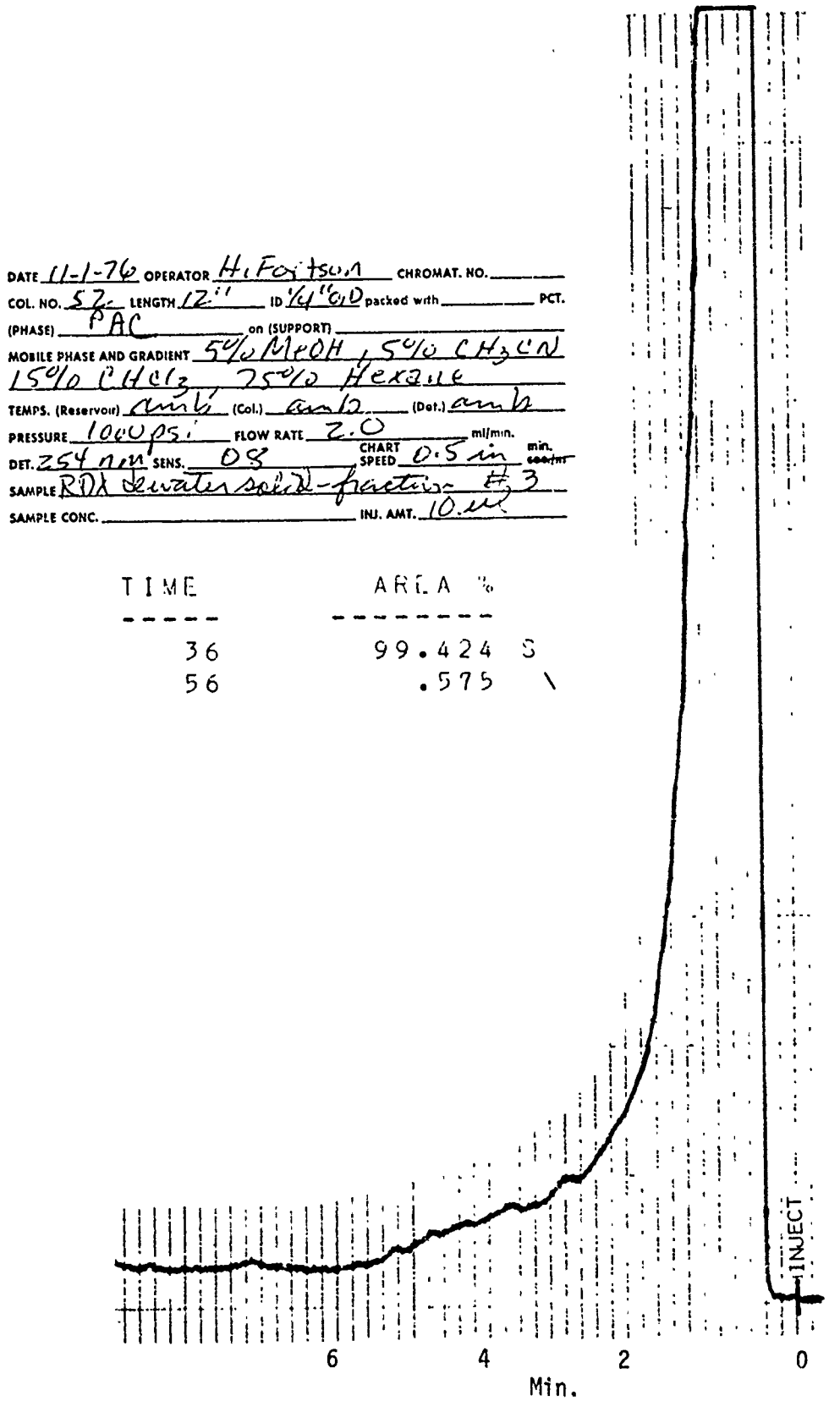


Figure C-3B. HPLC of Chromatogram of RDX Dewater Fraction No. 3

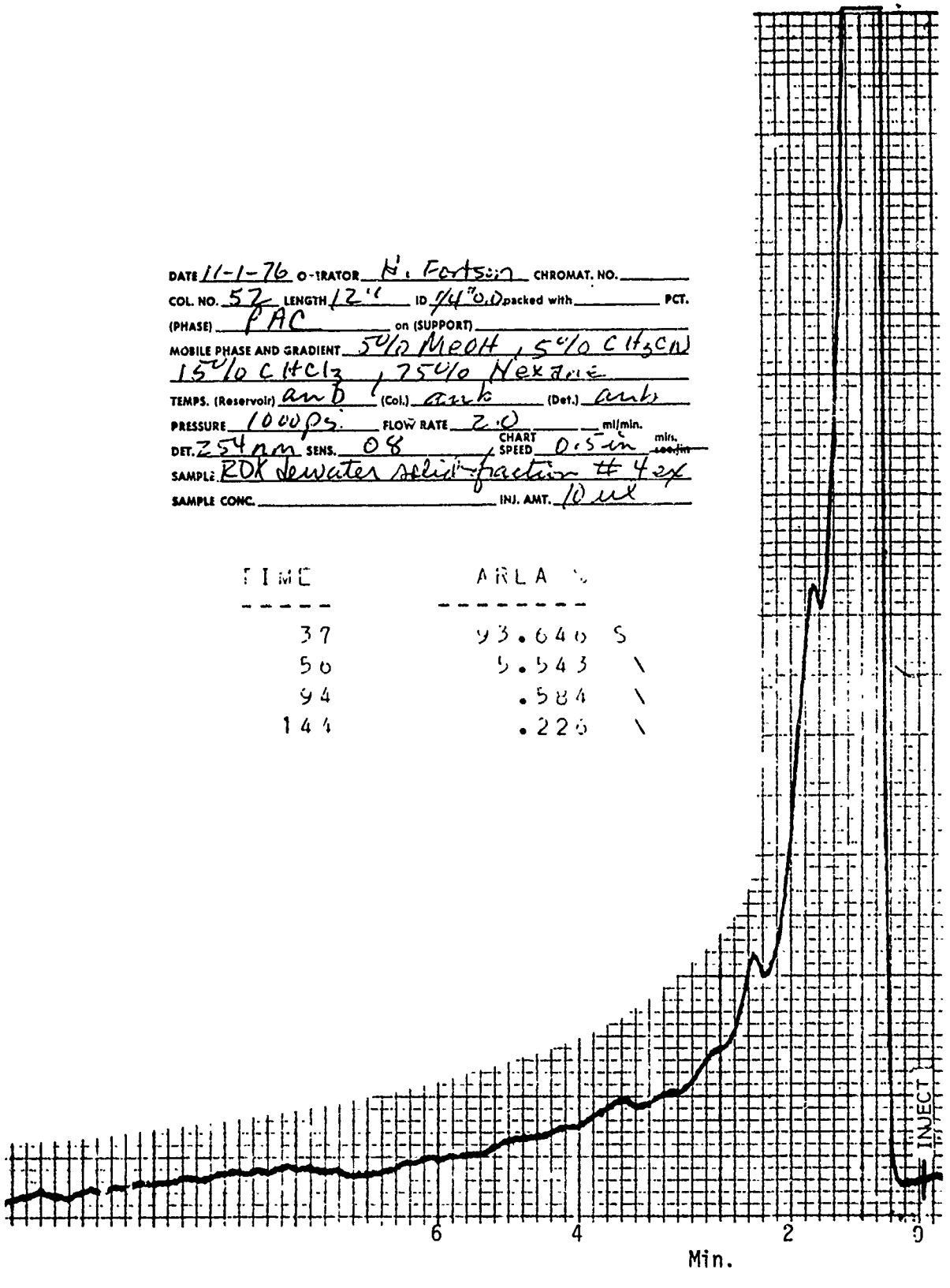


Figure C-4B. HPLC Chromatogram of RDX Dewater Fraction No. 4

DATE 11-1-76 OPERATOR H. Fortson CHROMAT. NO. _____

COL. NO. 52 LENGTH 12" ID 1/4" OD packed with _____ PCT.

(PHASE) PAC on (SUPPORT) _____

MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN, 15% $CHCl_3$, 75% Hexane

TEMPS. (Reservoir) amb (Col.) amb (Det.) amb

PRESSURE 1000 psi FLOW RATE 2.0 ml/min.

DET. 254 nm SENS. 08 CHART SPEED 0.5 in min.

SAMPLE RDX Dewater Solids fraction #5 ex

SAMPLE CONC. _____ INJ. AMT. 10 ul

TIME	AREA %	
40	22.105	T-
56	68.115	S
93	9.288	\
146	.490	\

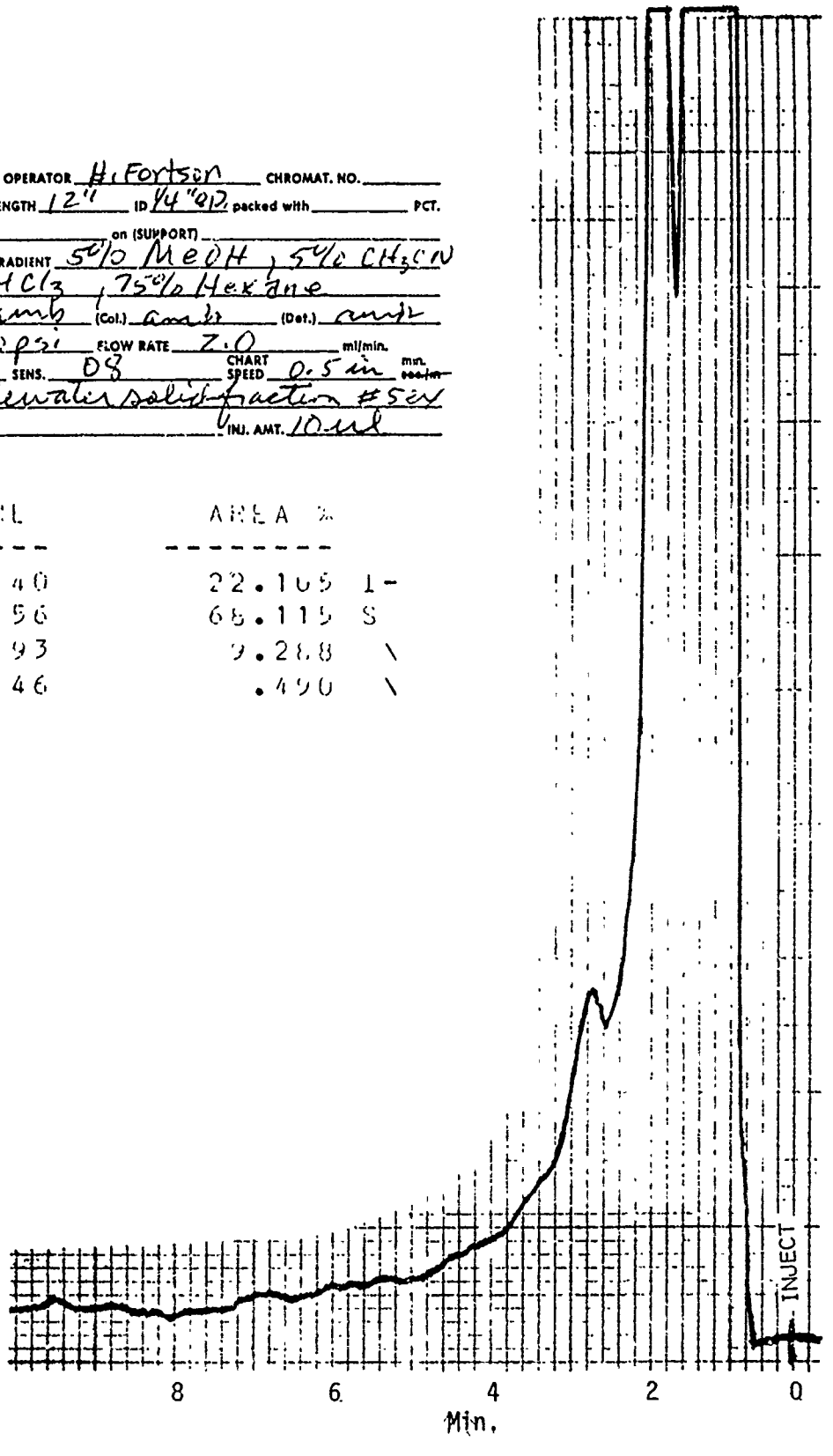


Figure C-5B. HPLC Chromatogram of RDX Dewater Fraction No. 5

DATE 11-1-76 OPERATOR H. Fortson CHROMAT. NO. _____

COL. NO. 52 LENGTH 12" ID 1/4" OD packed with _____ PCT.

(PHASE) PAC on (SUPPORT) _____

MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN, 15% $CHCl_3$, 75% Hexane

TEMPS. (Reservoir) amb (Col.) amb (Det.) amb

PRESSURE 1000 psi FLOW RATE 2.0 ml/min.

DET. 254 nm SENS. .05 CHART SPEED 0.5 in min. sec/in

SAMPLE RDX dewater solid - fraction #6

SAMPLE CONC. _____ INJ. AMT. 10 ul

TIME	AREA %	
28	.060	1-
36	.203	1-
86	.379	
144	99.356	
417	.000	S

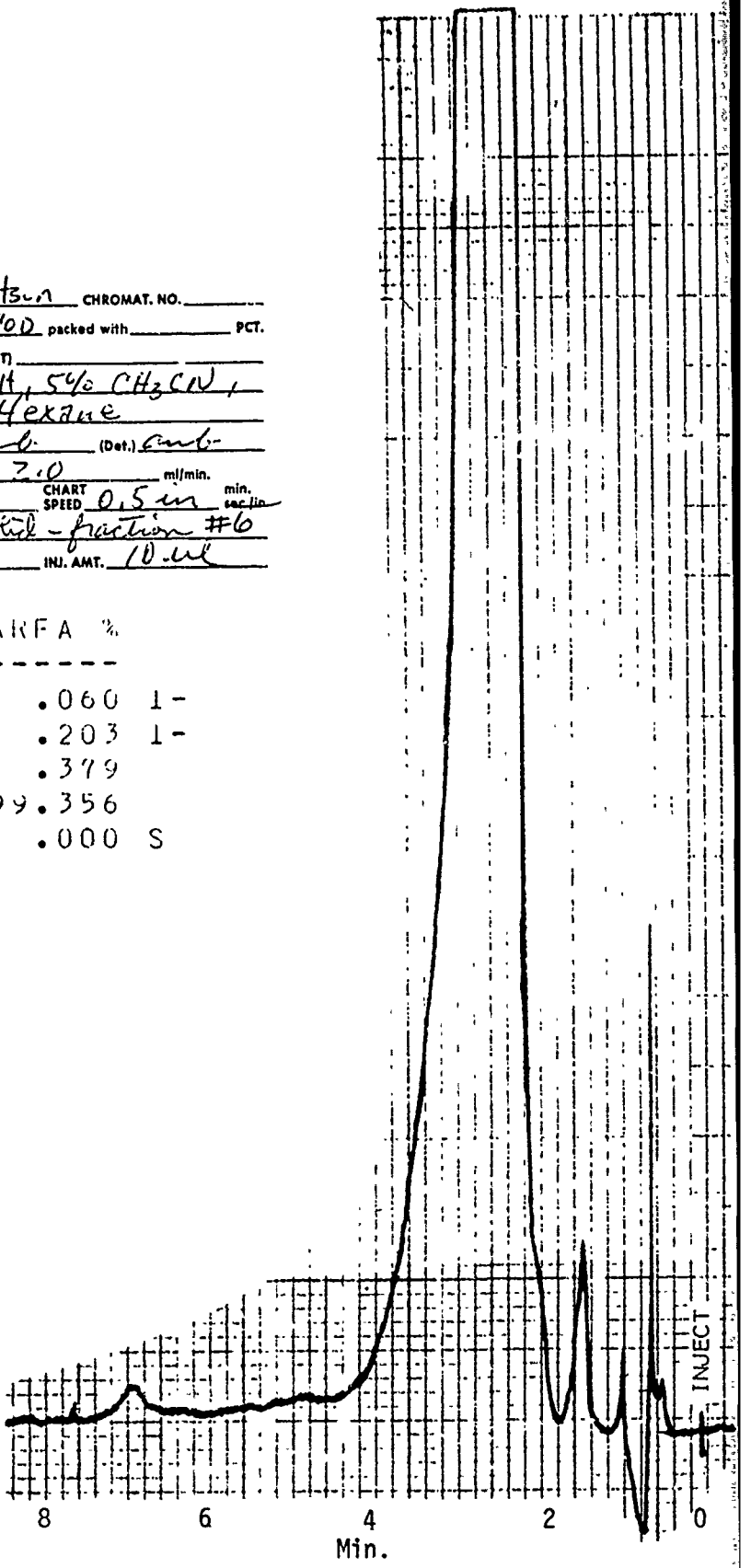


Figure C-6B. HPLC Chromatogram of RDX Dewater Fraction No. 6

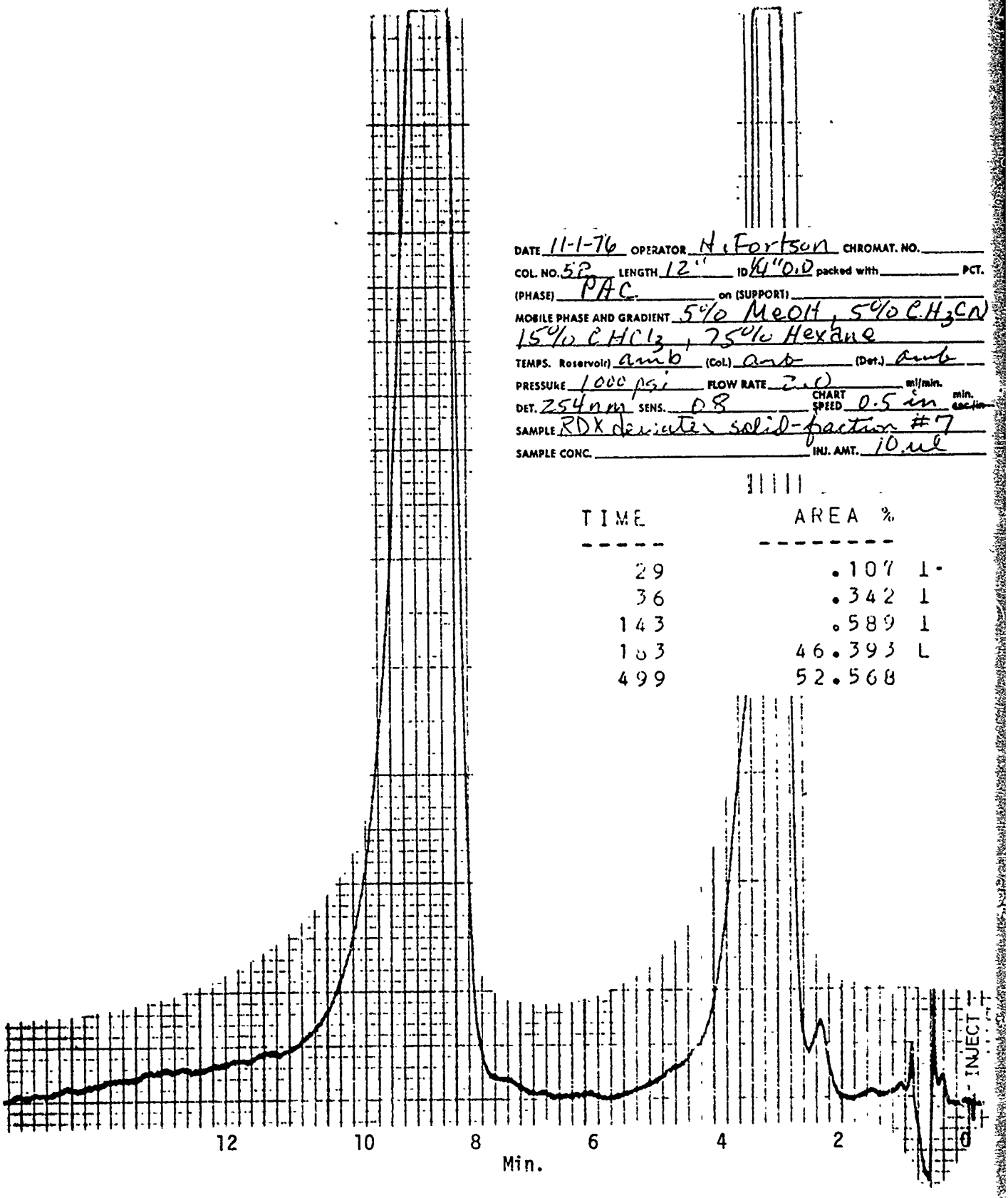


Figure C-7B. HPLC Chromatogram of RDX Dewater Fraction No. 7

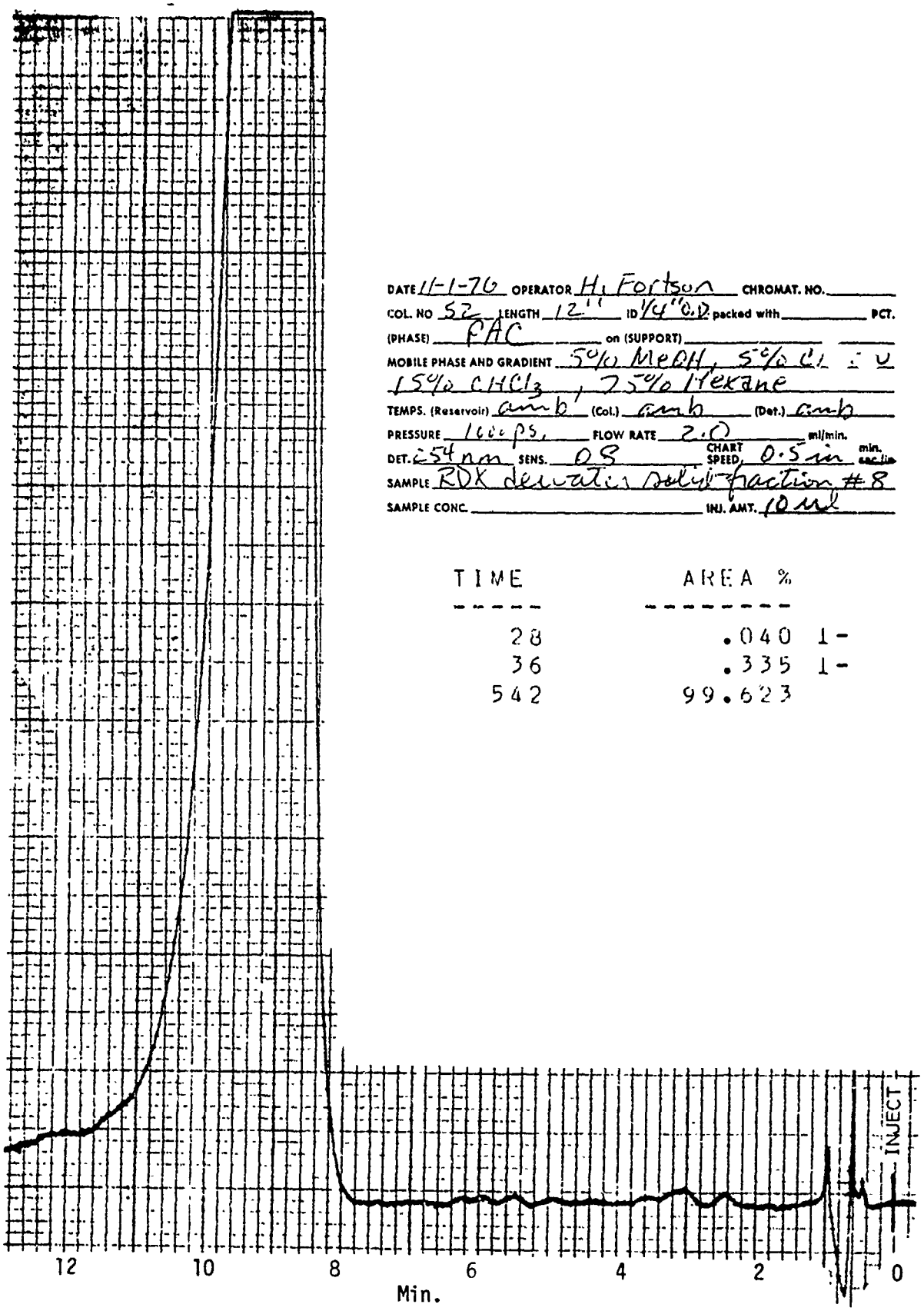


Figure C-8B. HPLC Chromatogram of RDX Dewater Fraction No. 8

DATE 11-1-76 OPERATOR H. Fortson CHROMAT. NO. _____
COL. NO. 544 LENGTH 12" ID 1/4" OD packed with _____ PCT.
(PHASE) DiOL on (SUPPORT) _____
MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN
15% $CHCl_3$, 75% Hexane
TEMPS. (Reservoir) Amb (Col.) Amb (Det.) Amb
PRESSURE 260 psi FLOW RATE 2.0 ml/min.
DET. 254 nm SENS. .08 CHART SPEED 0.5 cm/min
SAMPLE RDX dewater solid fraction #1
SAMPLE CONC. _____ INJ. AMT. 10 ul

TIME	AREA %	
123	94.940	S
157	1.461	\
217	2.196	\
227	1.400	\

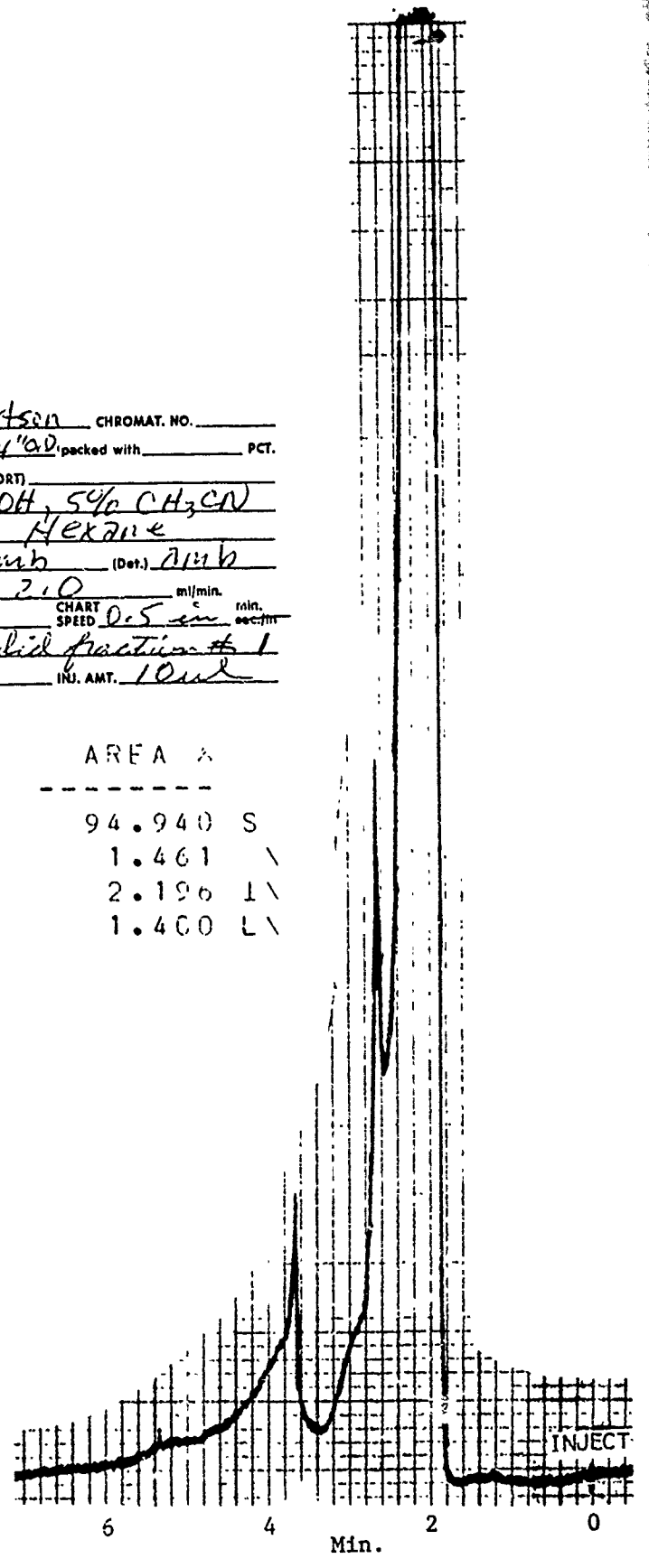


Figure C-9B. HPLC Chromatogram of RDX Dewater Fraction No. 1

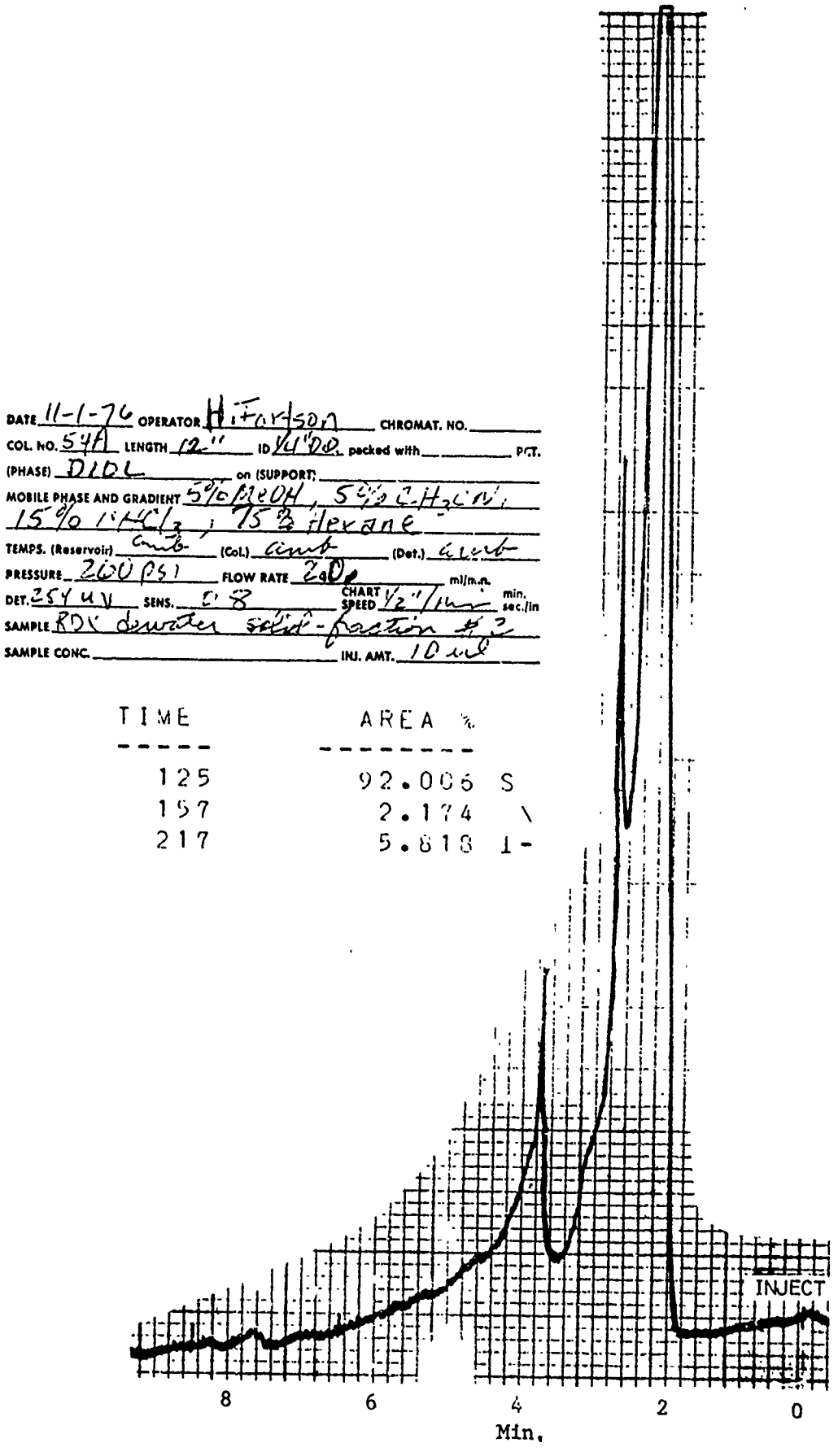


Figure C-10B. HPLC Chromatogram of RDX Dewater Fraction No. 2

DATE 11-1-76 OPERATOR H. D. Fortson CHROMAT. NO. _____
COL. NO. 54A LENGTH 12' ID 1/4" O.D. packed with _____ PCT.
(PHASE) Diol on (SUPPORT) _____
MOBILE PHASE AND GRADIENT 5% MeOH, 5% CH_3CN
15% $CHCl_3$, 75% Hexane
TEMPS. (Reservoir) Amb (Col.) Amb (Det.) Amb
PRESSURE 260 psi FLOW RATE 2.0 ml/min.
DET. 254 nm SENS. .08 CHART SPEED 0.5 in/min.
SAMPLE RDX dewater solid fraction #3
SAMPLE CONC. _____ INJ. AMT. 10 ul

TIME	AREA %	
151	44.932	I-
160	53.079	S
223	1.987	\

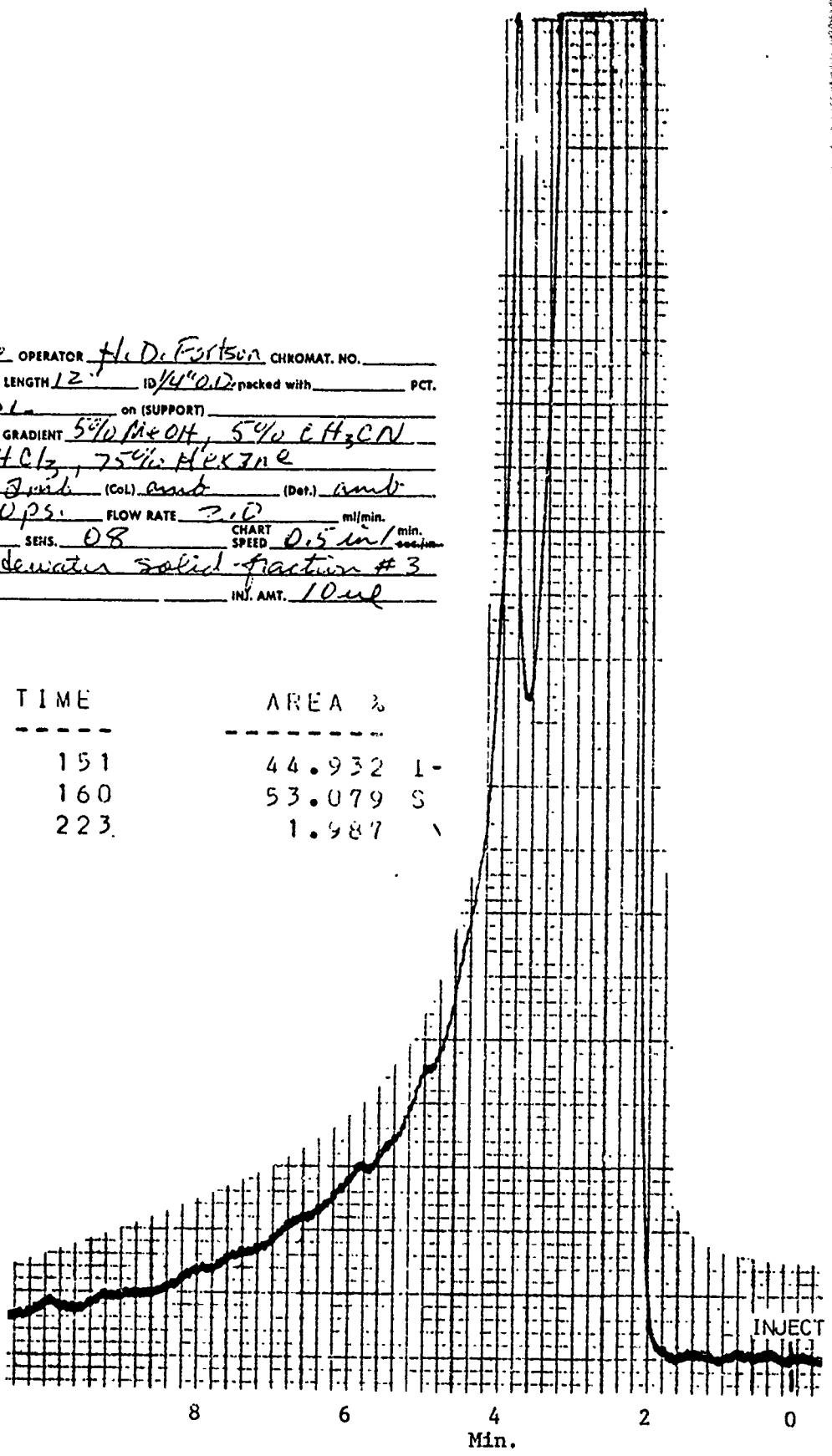


Figure C-11B. HPLC Chromatogram of RDX Dewater Fraction No. 3

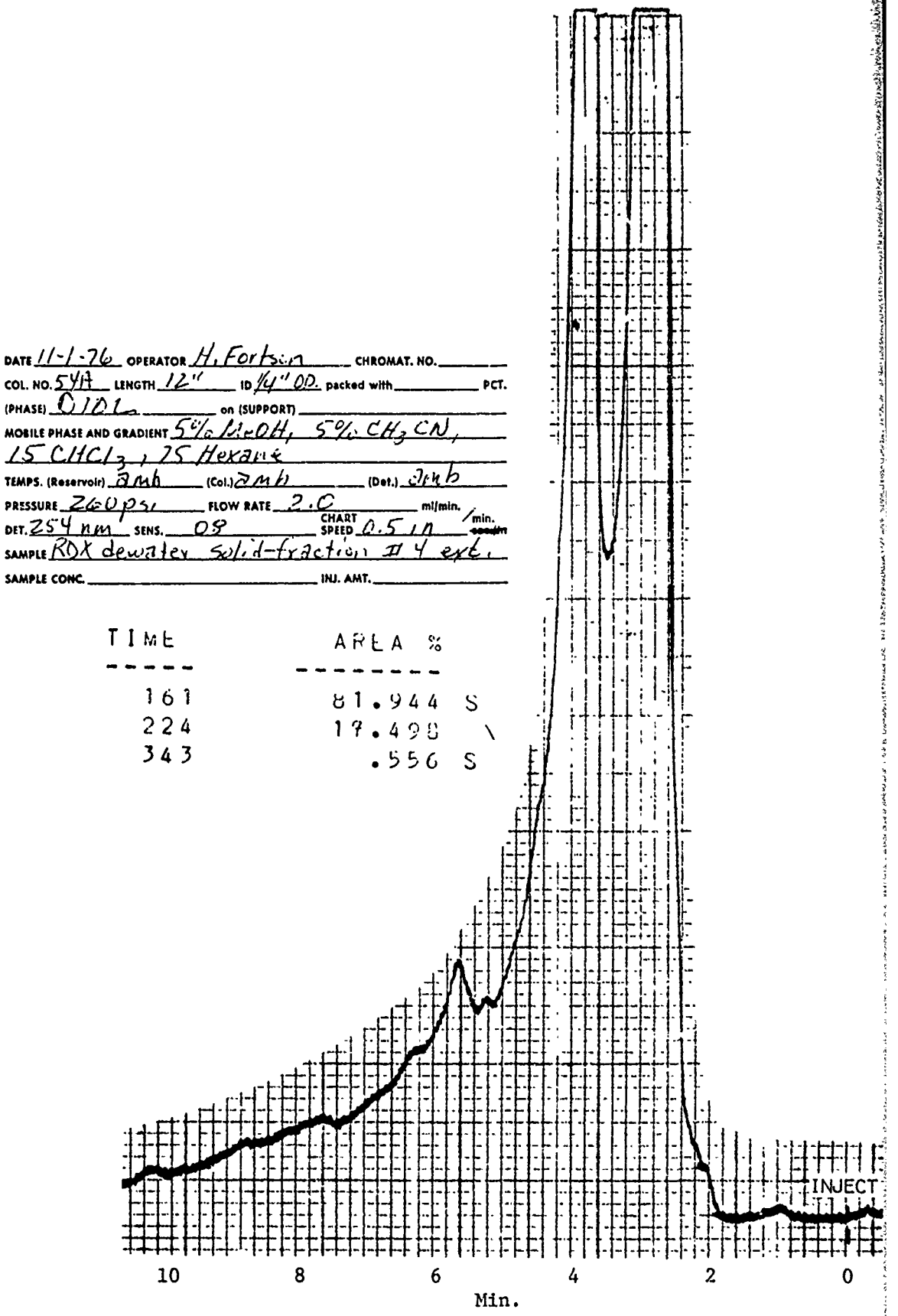


Figure C-12B. HPLC Chromatogram of RDX Dewater Fraction No. 4

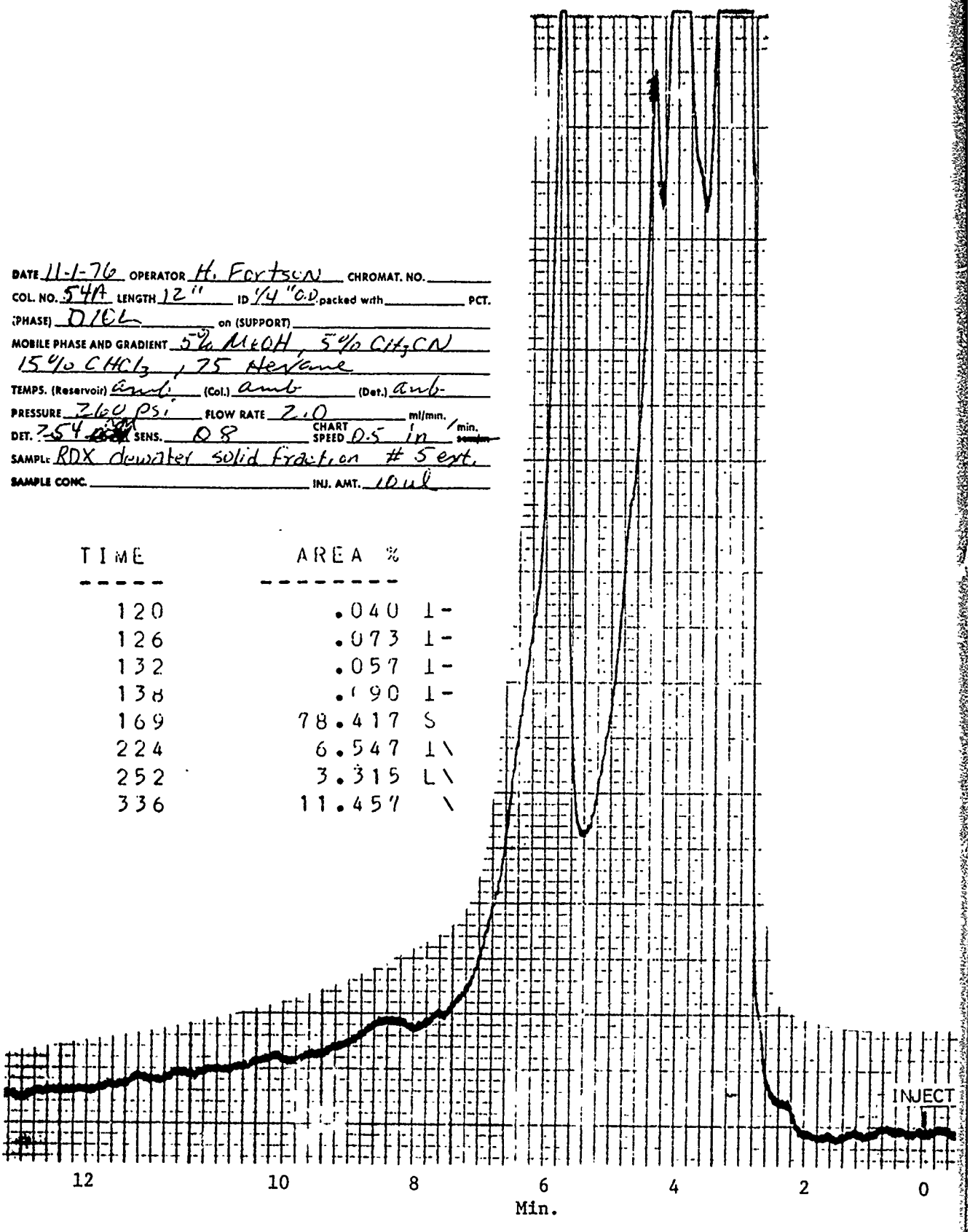
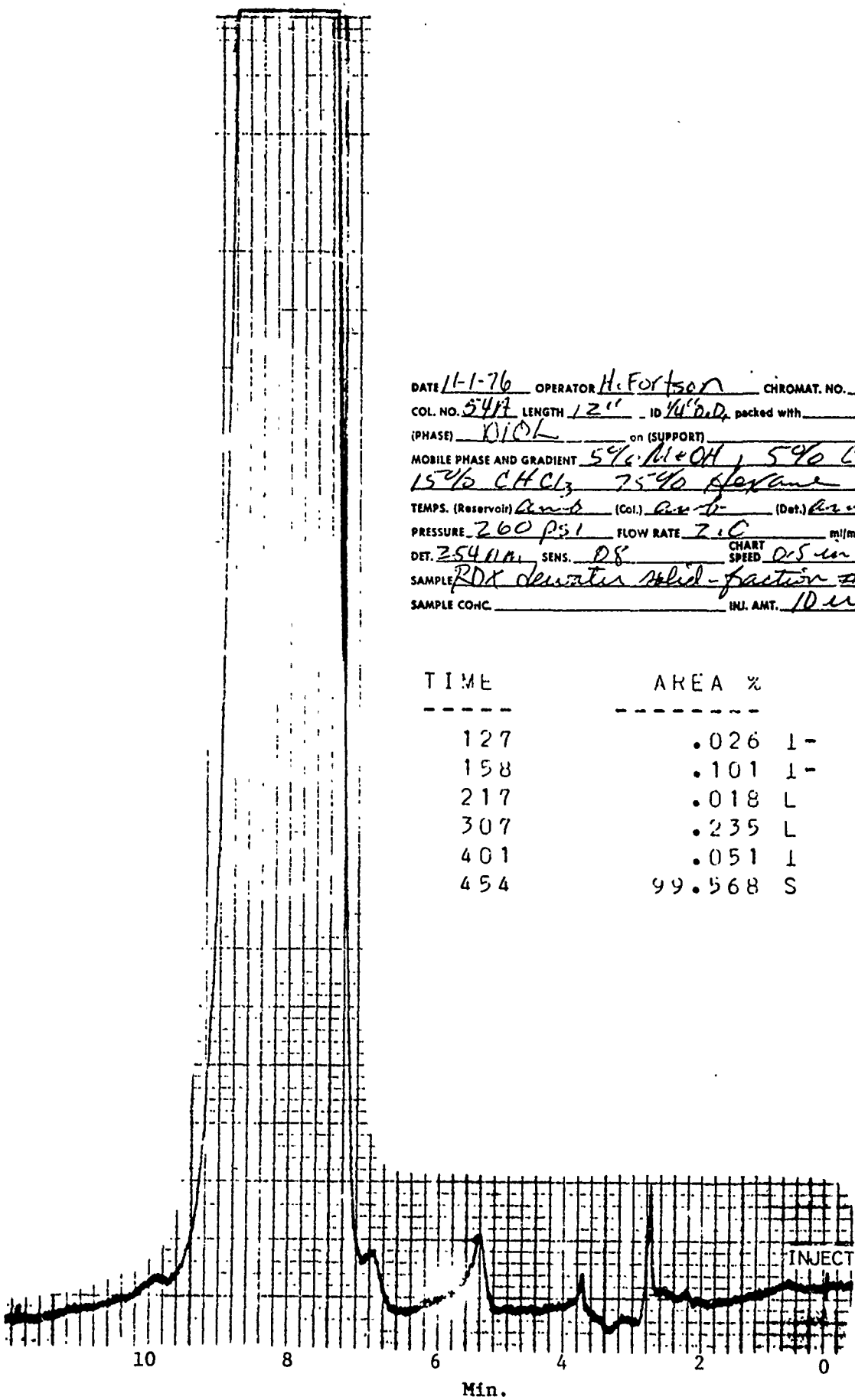


Figure C-13B. HPLC Chromatogram of RDX Dewater Fraction No. 5



DATE 11-1-76 OPERATOR H. Fortson CHROMAT. NO. _____

COL. NO. 5417 LENGTH 12" ID 1/4" O.D. packed with _____ PCT.

(PHASE) DIOL on (SUPPORT) _____

MOBILE PHASE AND GRADIENT 5% MeOH / 5% CH_3CN / 15% $CHCl_3$ / 75% Hexane

TEMPS. (Reservoir) Amb (Col.) Amb (Det.) Amb

PRESSURE 260 psi FLOW RATE 2.0 ml/min.

DET. 254 nm SENS. .08 CHART SPEED .5 cm/min.

SAMPLE RDX dewater solid - fraction #6

SAMPLE CONC. _____ INJ. AMT. 10 µl

TIME	AREA %	
127	.026	T-
158	.101	T-
217	.018	L
307	.235	L
401	.051	T
454	99.568	S

Figure C-14B. HPLC Chromatogram of RDX Dewater Fraction No. 6

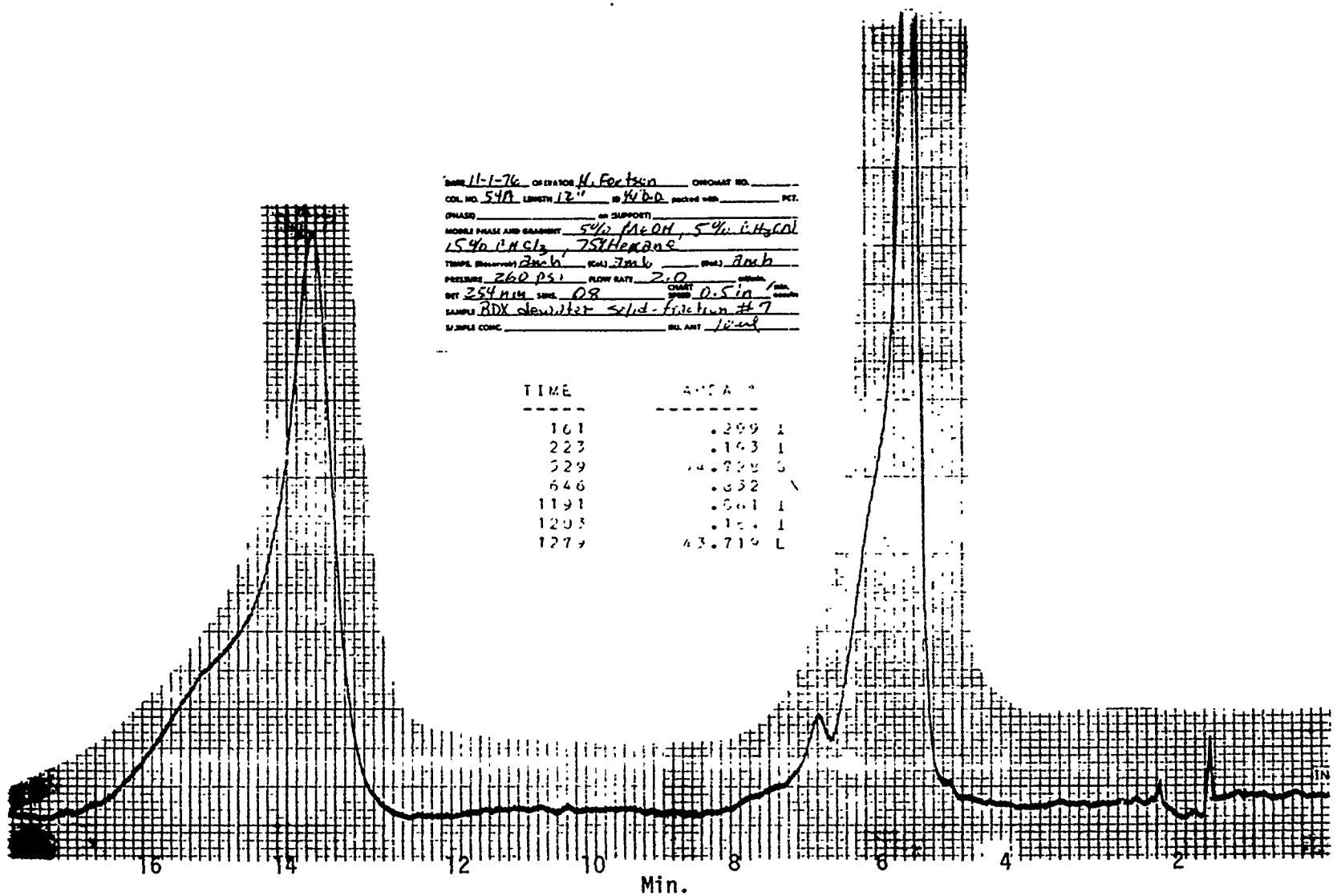


Figure C-15B. HPLC Chromatogram of RDX Dewater Fraction No. 7

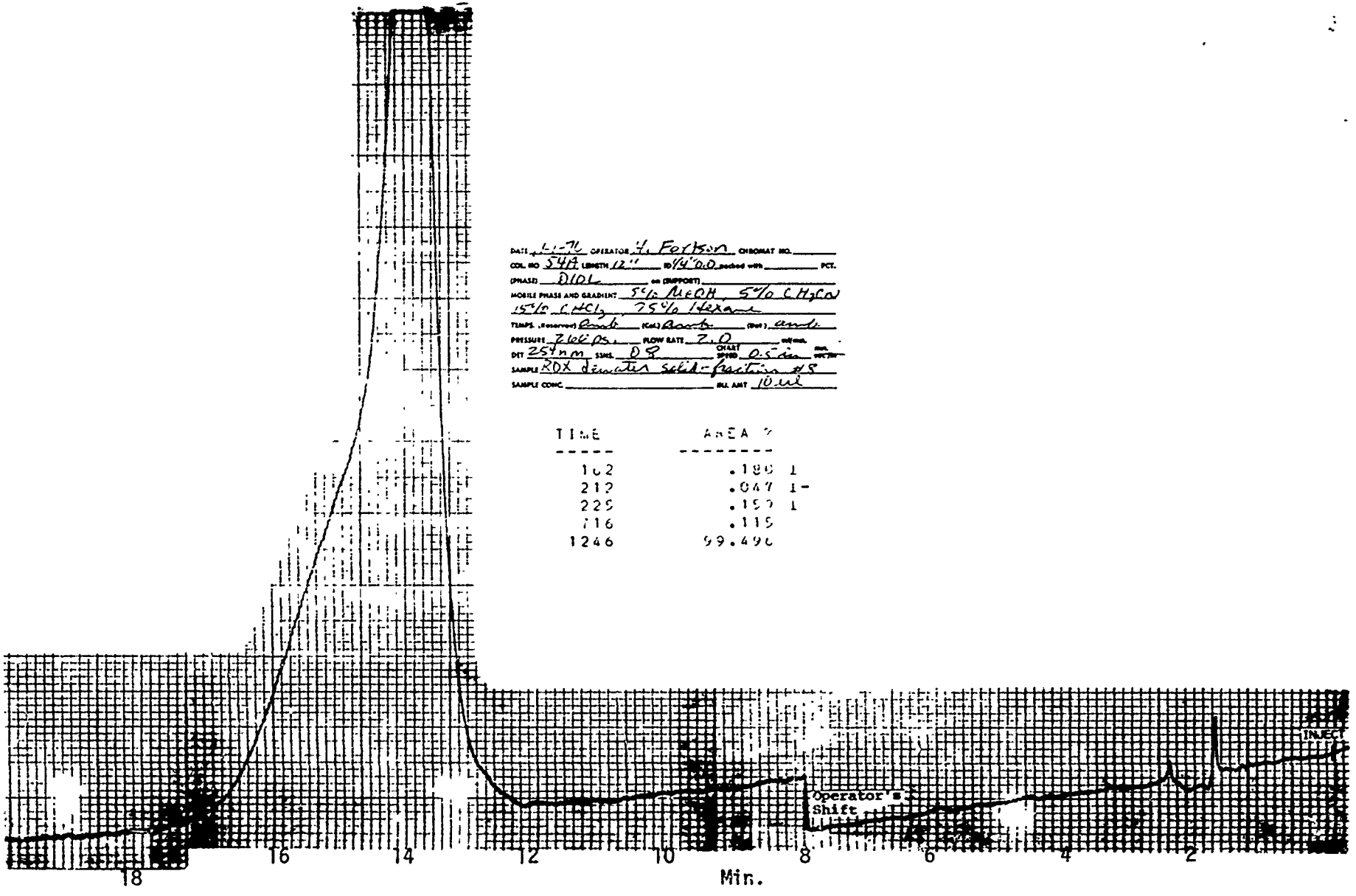


Figure C-16B. HPLC Chromatogram of RDX Dewater Fraction No. 8

Figures C-1C and C-2C

HIGH PERFORMANCE LIQUID CHROMATOGRAMS OF RDX DEWATER SOLIDS
AND HMX DEWATER SOLIDS

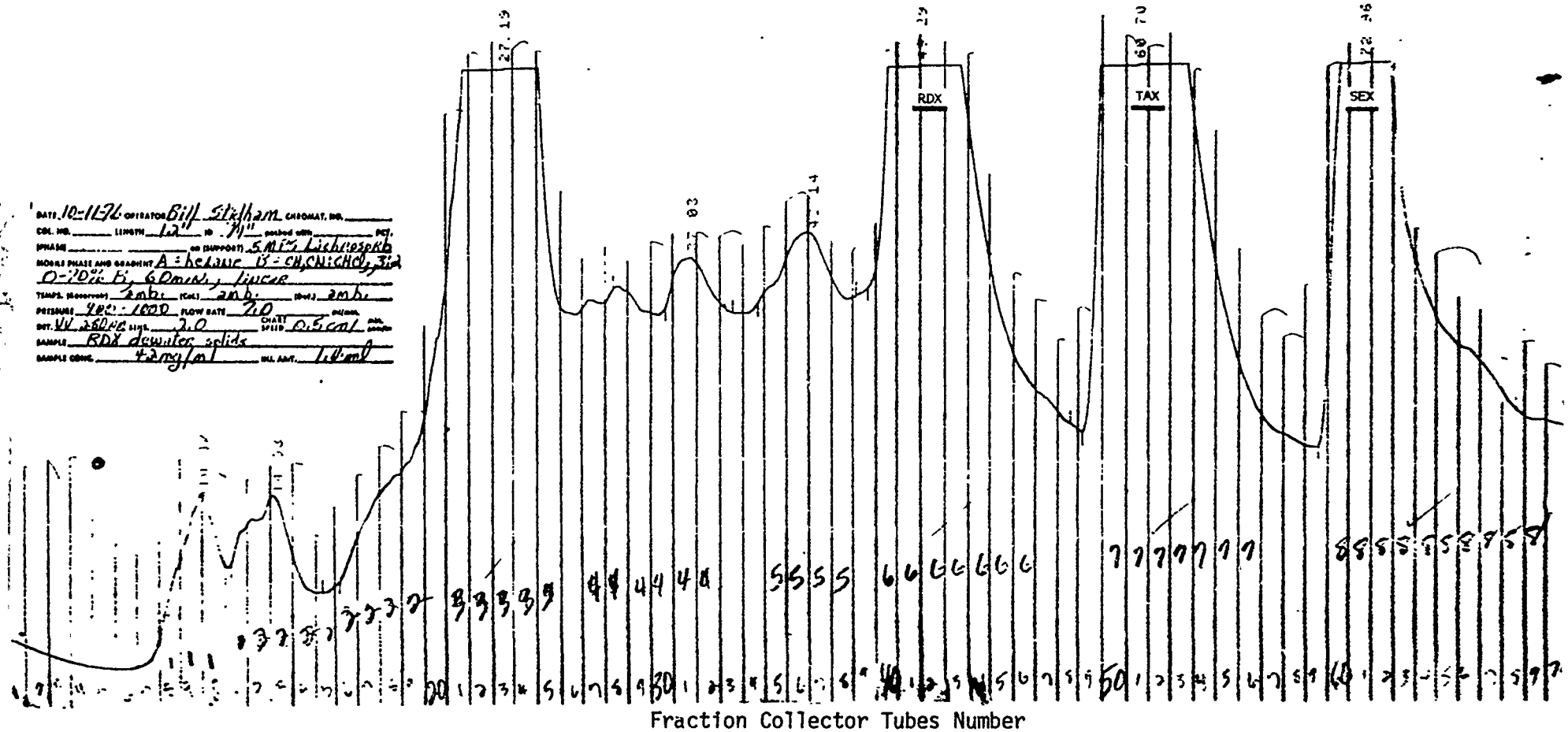


Figure C-1C. HPLC Chromatogram of RDX Dewater Solids

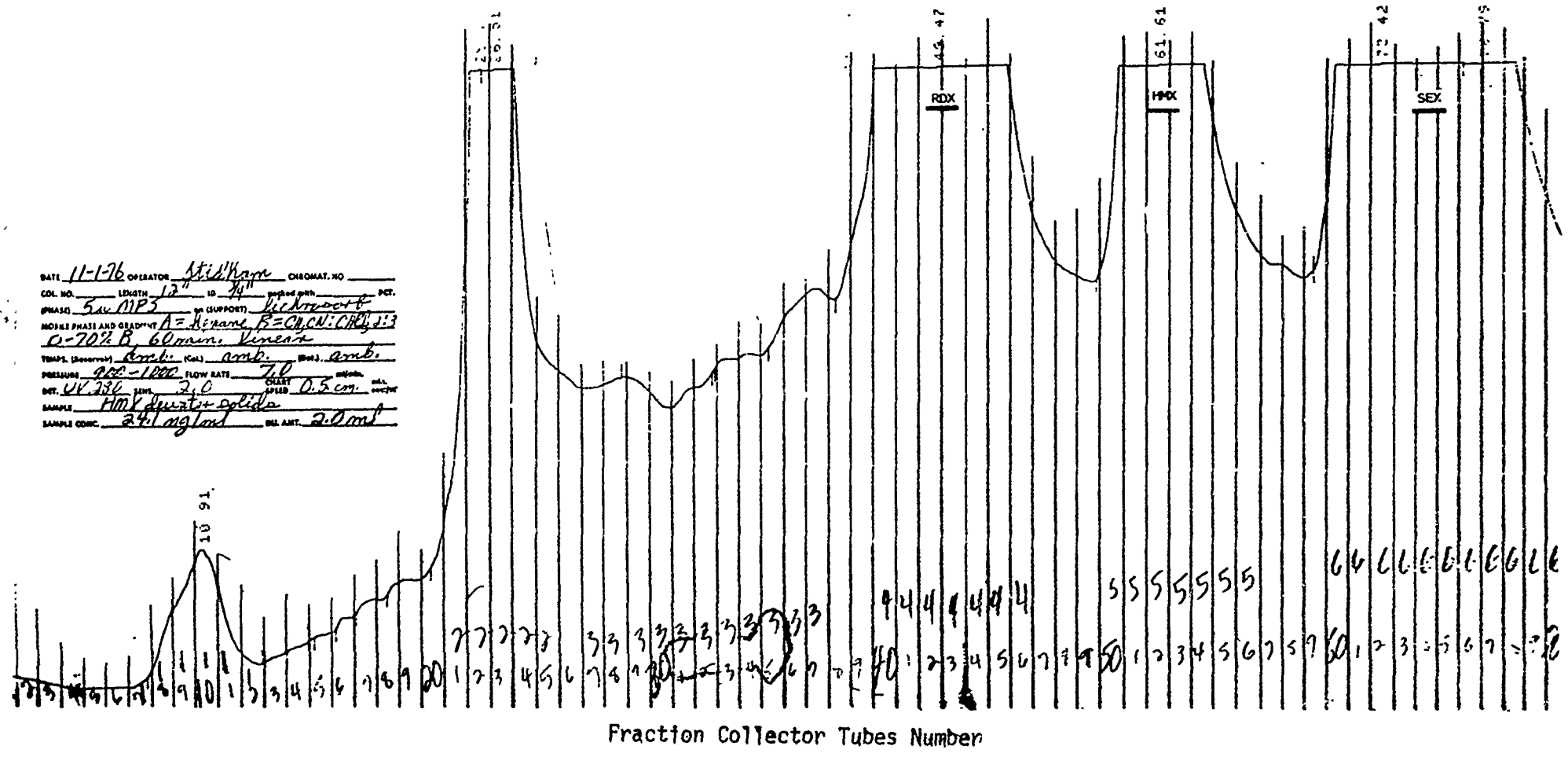
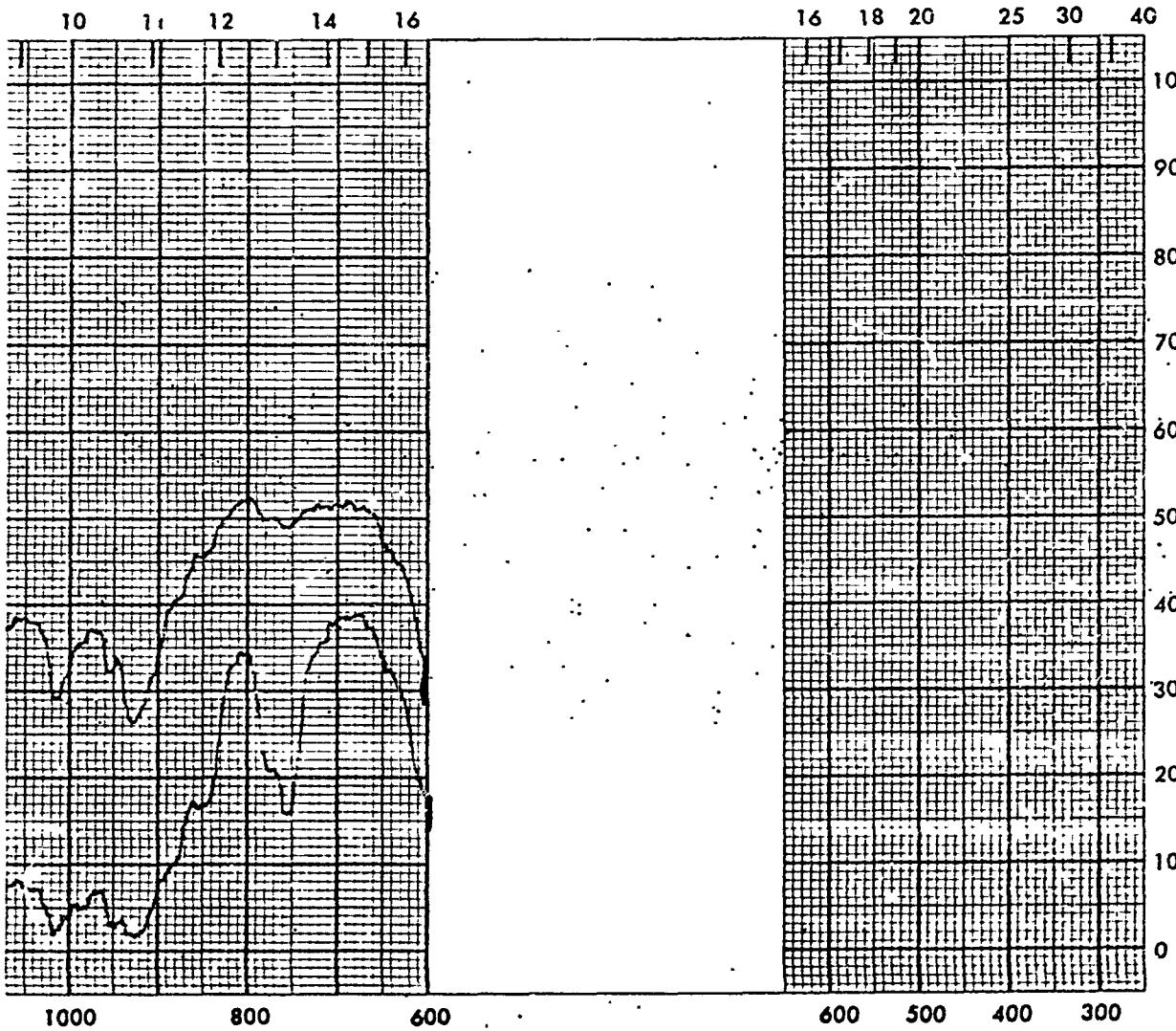


Figure C-2C. HPLC Chromatogram of HMX Dewater Solids

TS INC. FULLERTON, CALIFORNIA U.S.A.



SPECTRUM NO. 4946
DATE 21 OCT 1976
SAMPLE CCl4 SOLUBLES
1009-67-6
VISCOUS RED/BROWN SEMI-SOLID
SOURCE
STRUCTURE

PATH mm
SOLVENT
CONCENTRATION 1036-10/11
PHASE SMEAR/MELT
COMMENTS

ANALYST

Beckman®
INFRARED
SPECTROPHOTOMETER

Figure C-2D. IR Spectrum of RDX Dewater Fraction No. 6

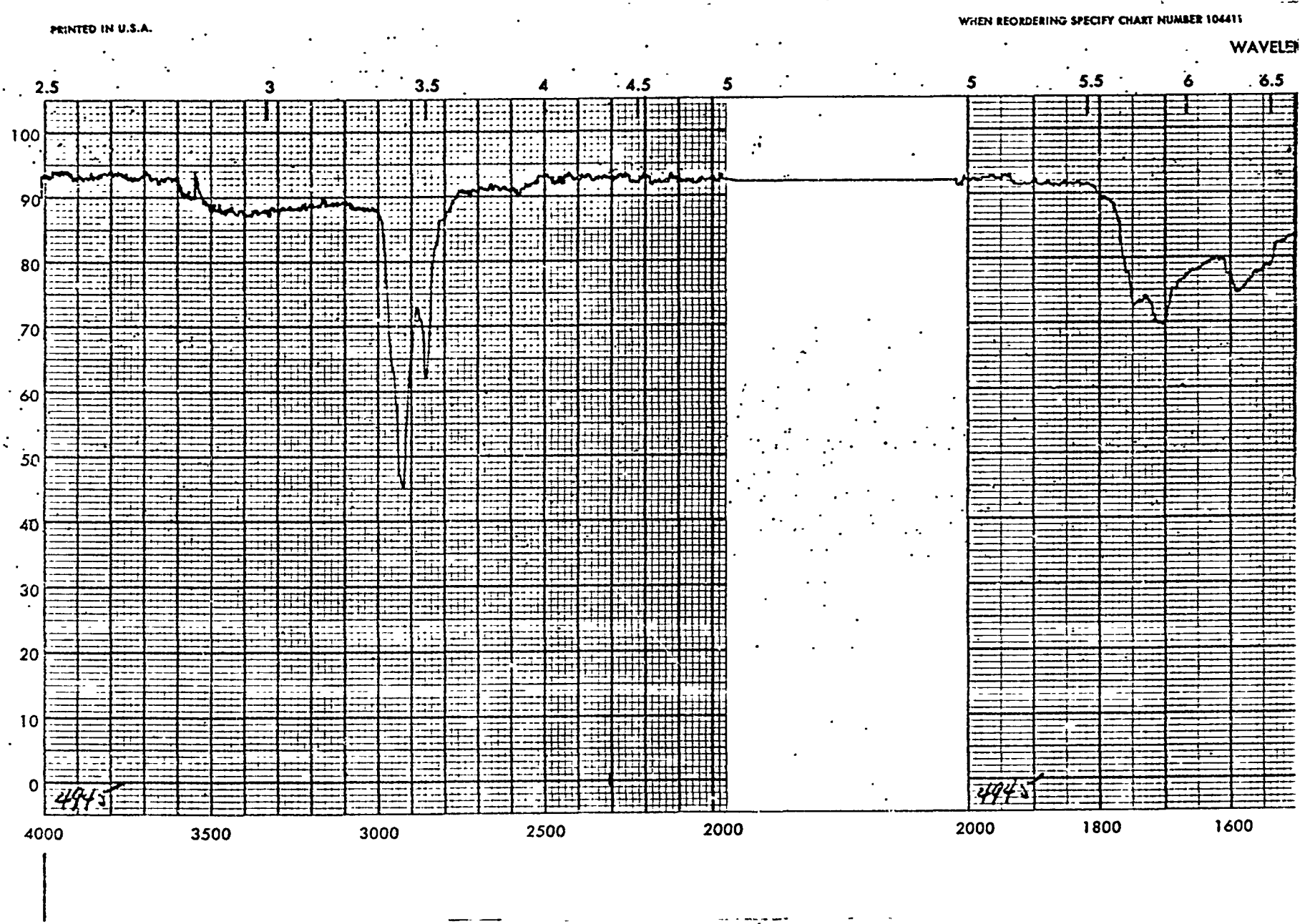


Figure C-1D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

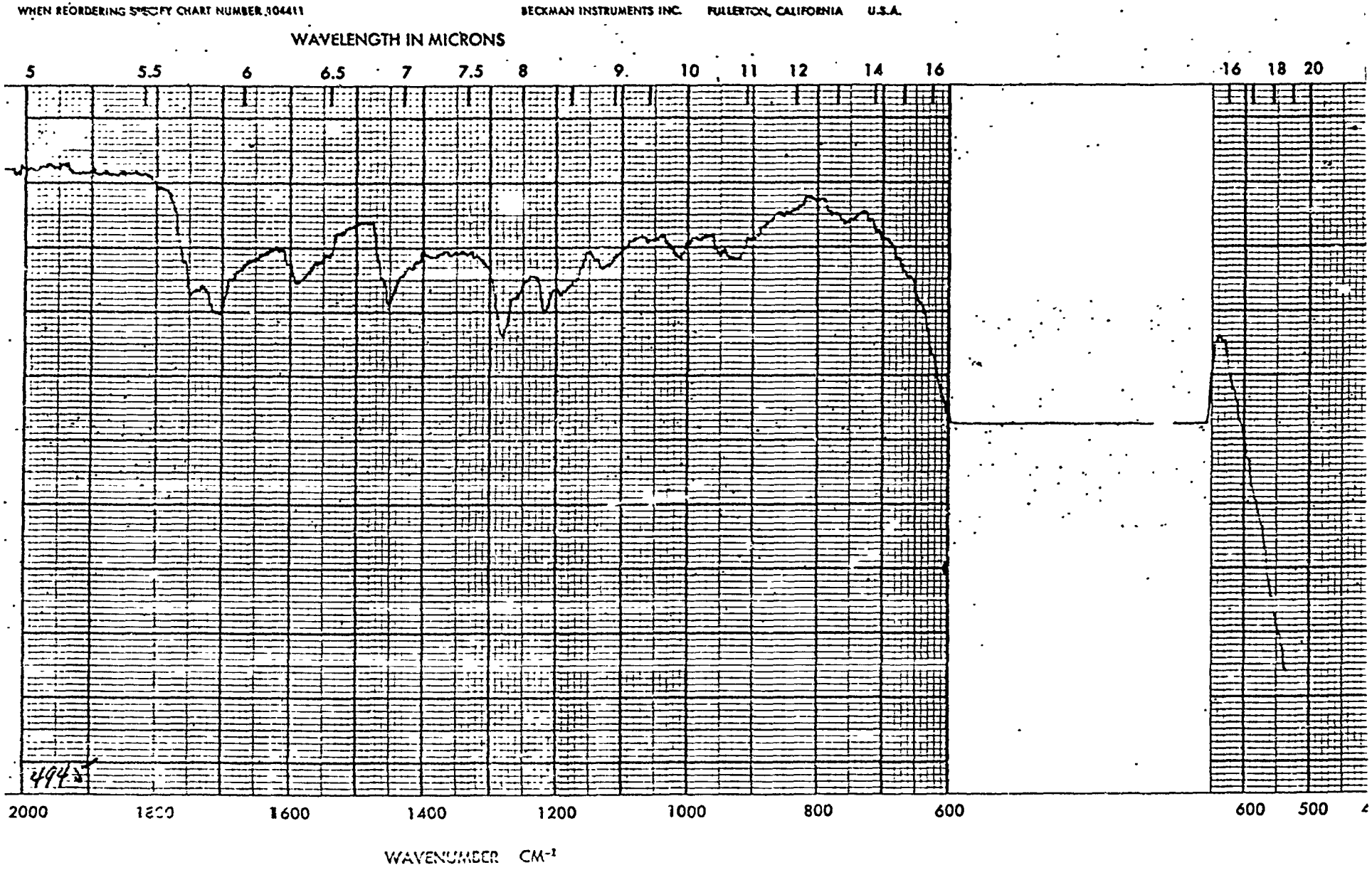


Figure C-1D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

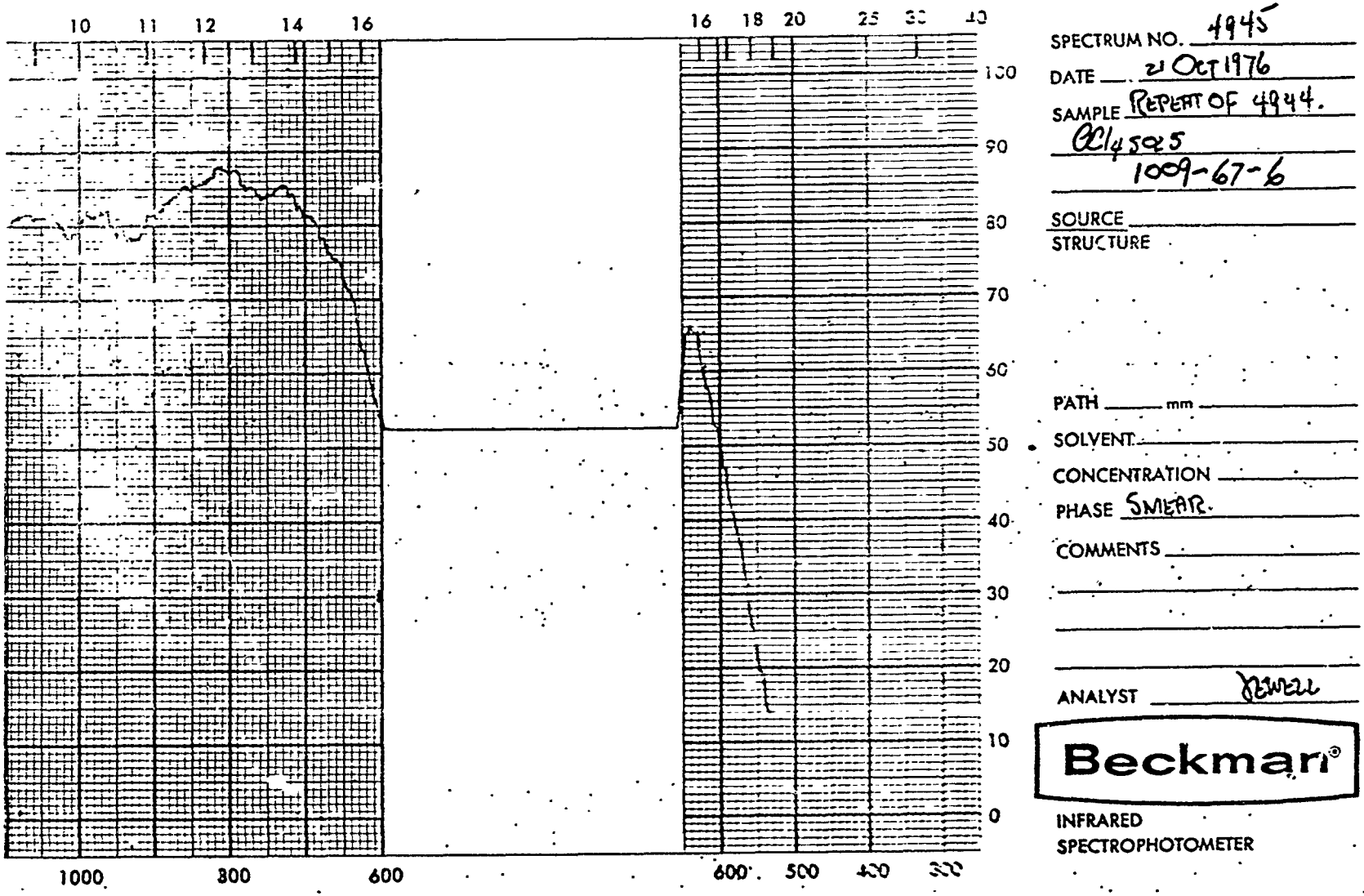


Figure C-1D. IR Spectrum of RDX Dewater Fraction No. 6

Figures C-1D to C-16D

IR SPECTRA OF DEWATER FRACTIONS AND REFERENCE COMPOUNDS

Pages 111 to 159

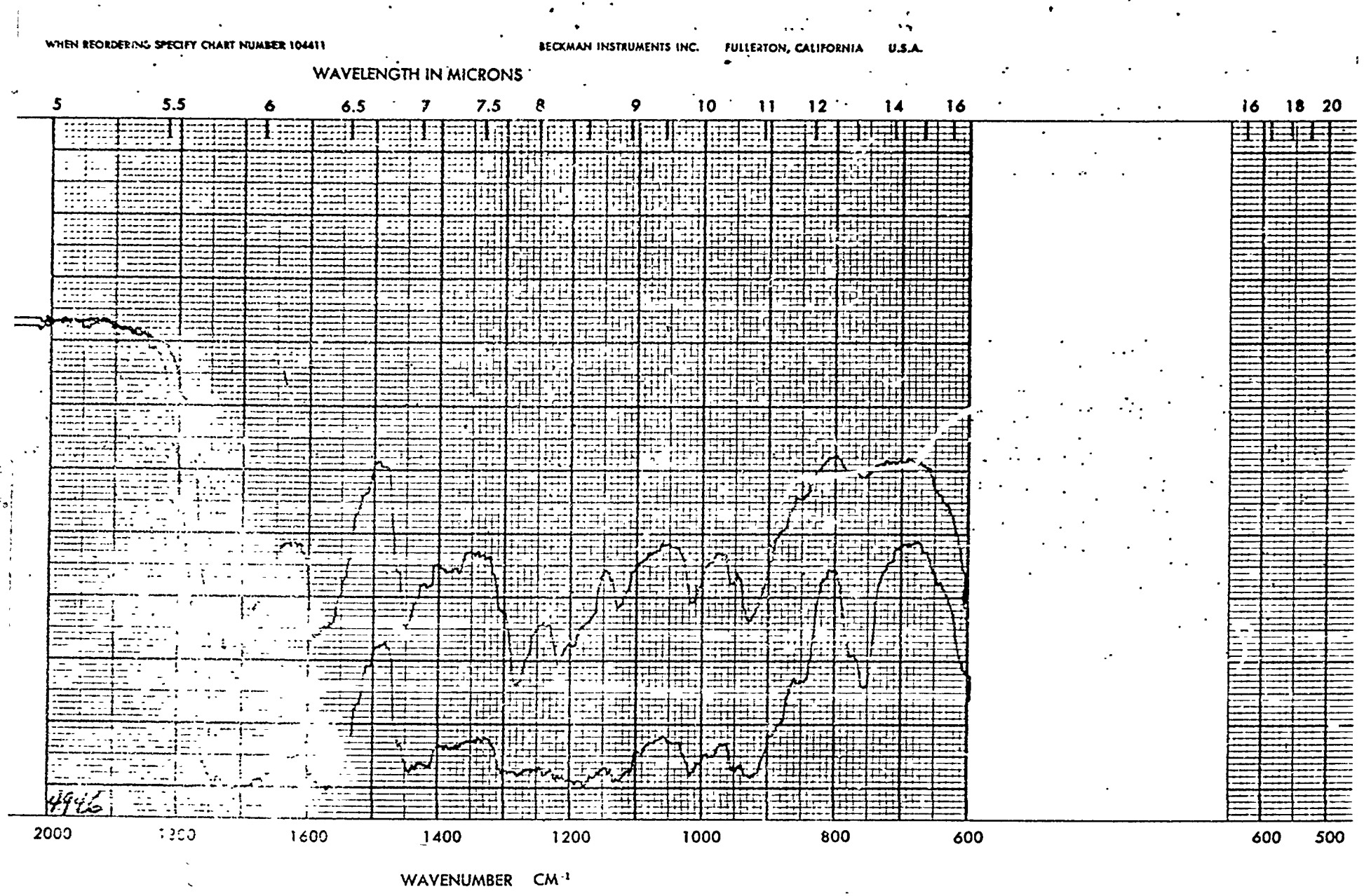


Figure C-2D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

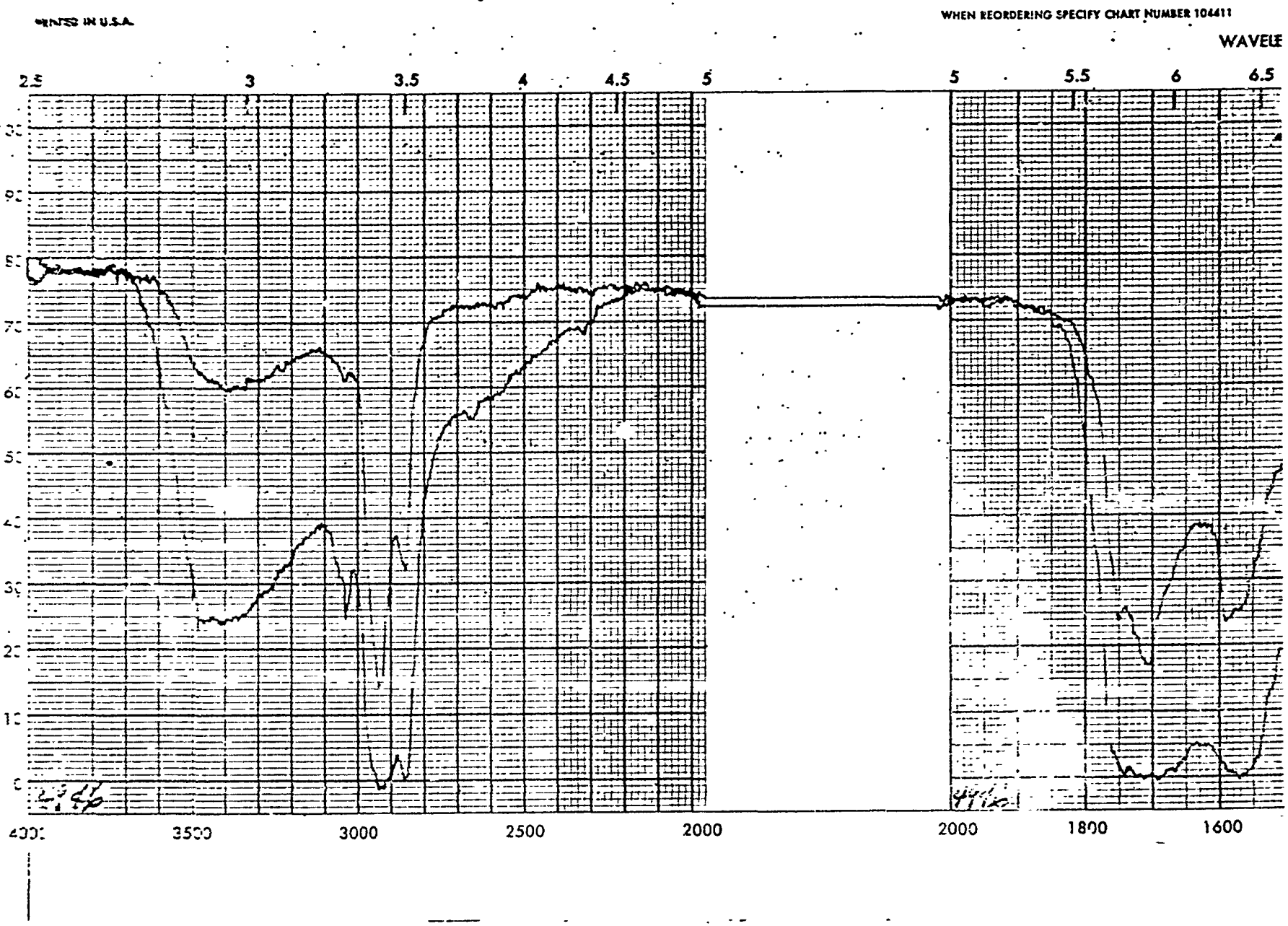


Figure C-2D (Continued). IR Spectrum of RDX Dewater Fraction No 6

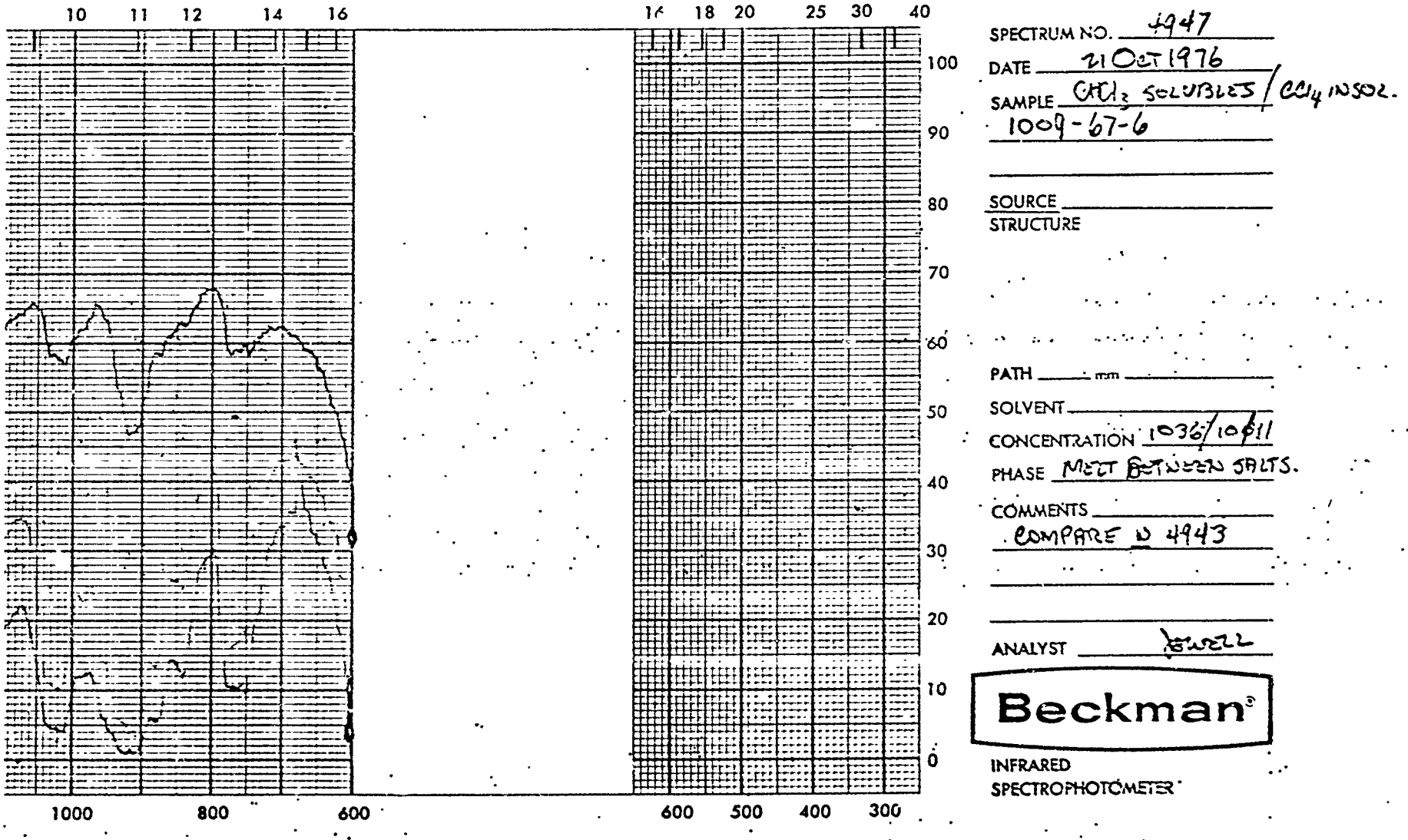


Figure C-3D. IR Spectrum of RDX Dewater Fraction No. 6

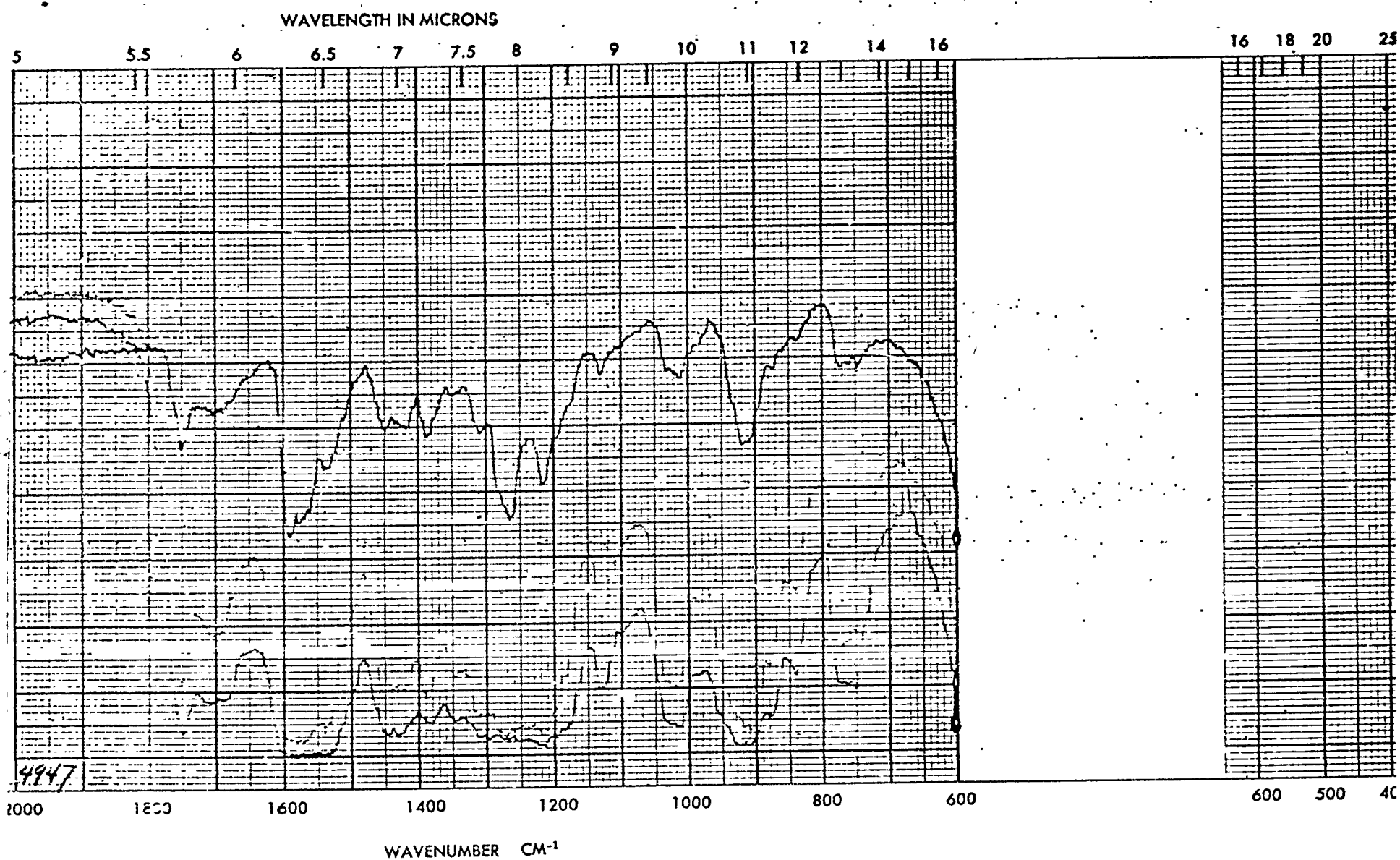


Figure C-3D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

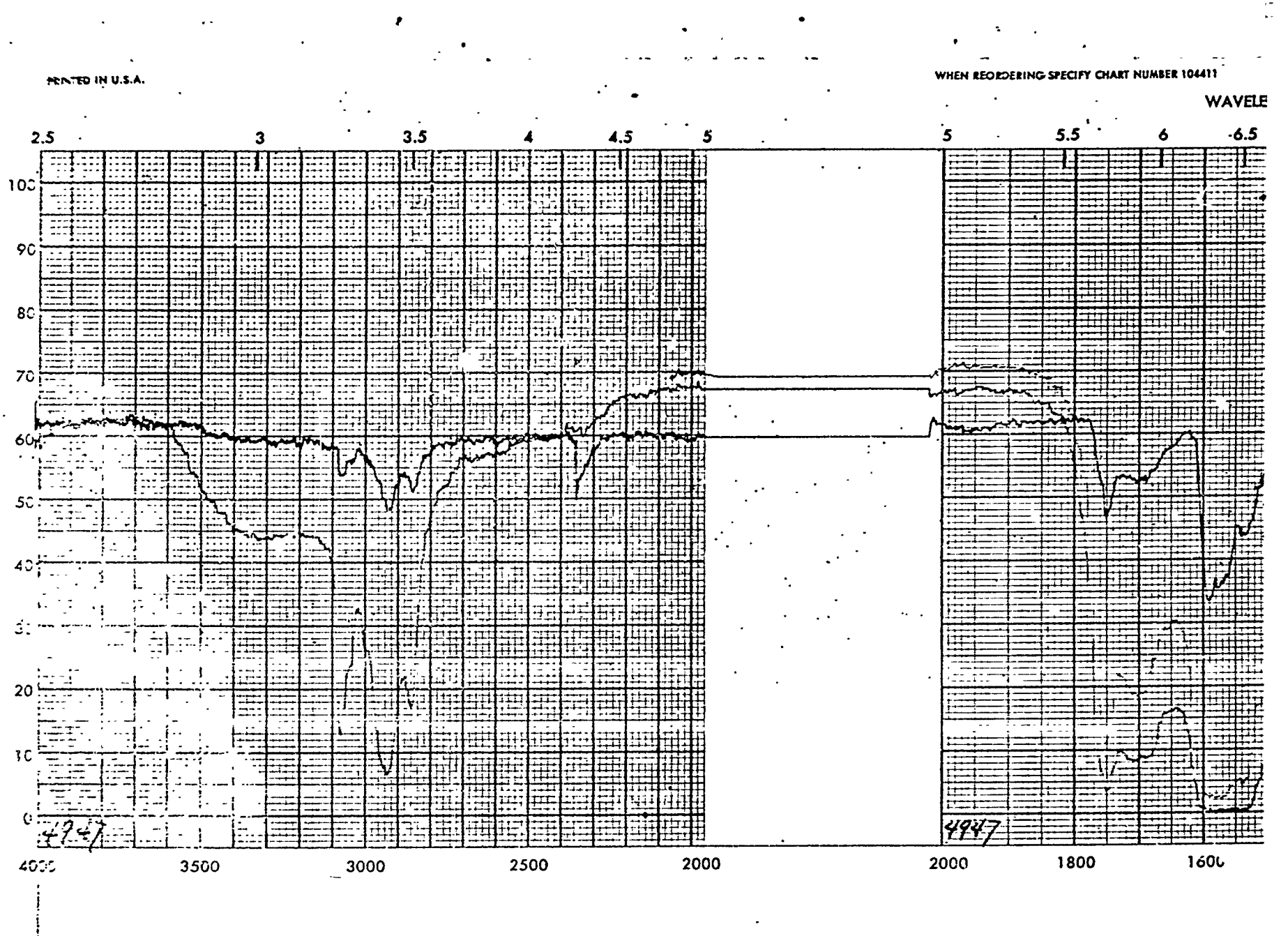
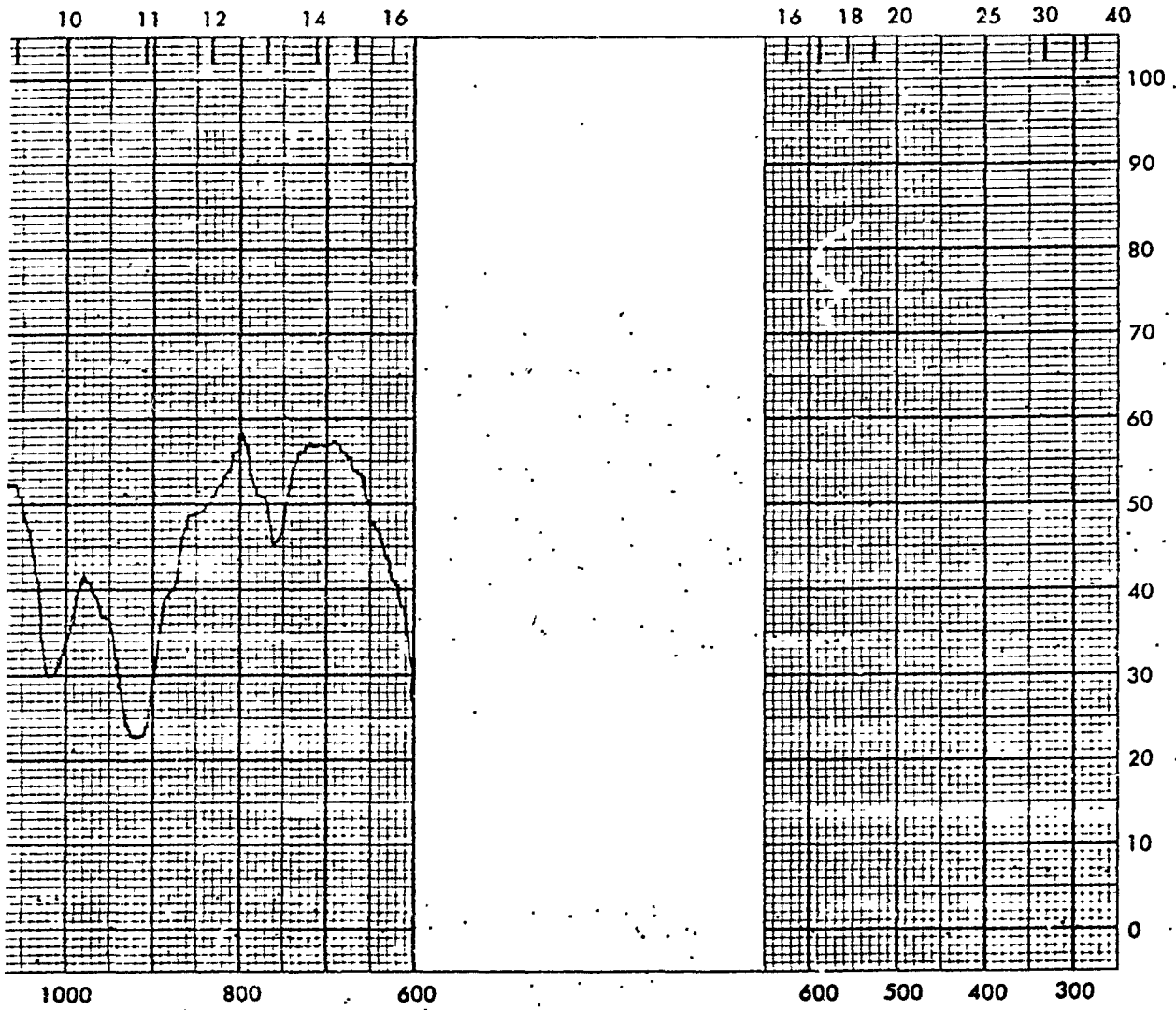


Figure C-3D (Continued).. IR Spectrum of RDX Dewater Fraction No. 6

S INC. FULLERTON, CALIFORNIA U.S.A.



SPECTRUM NO. 4943
DATE 20 Oct 76
SAMPLE CCl_4 INSOLS FROM 1009-67-6
REDDISH-BROWN
SOURCE 1036-11 VIAL
STRUCTURE

PATH ____ mm
SOLVENT
CONCENTRATION
PHASE HIGH MELT ZnW SALTS
COMMENTS COMPARE W 4947.
SEE ALSO PNX 4998

ANALYST KEWELL

Beckman®
INFRARED
SPECTROPHOTOMETER

Figure C-4D. IR Spectrum of RDX Dewater Fraction No. 6

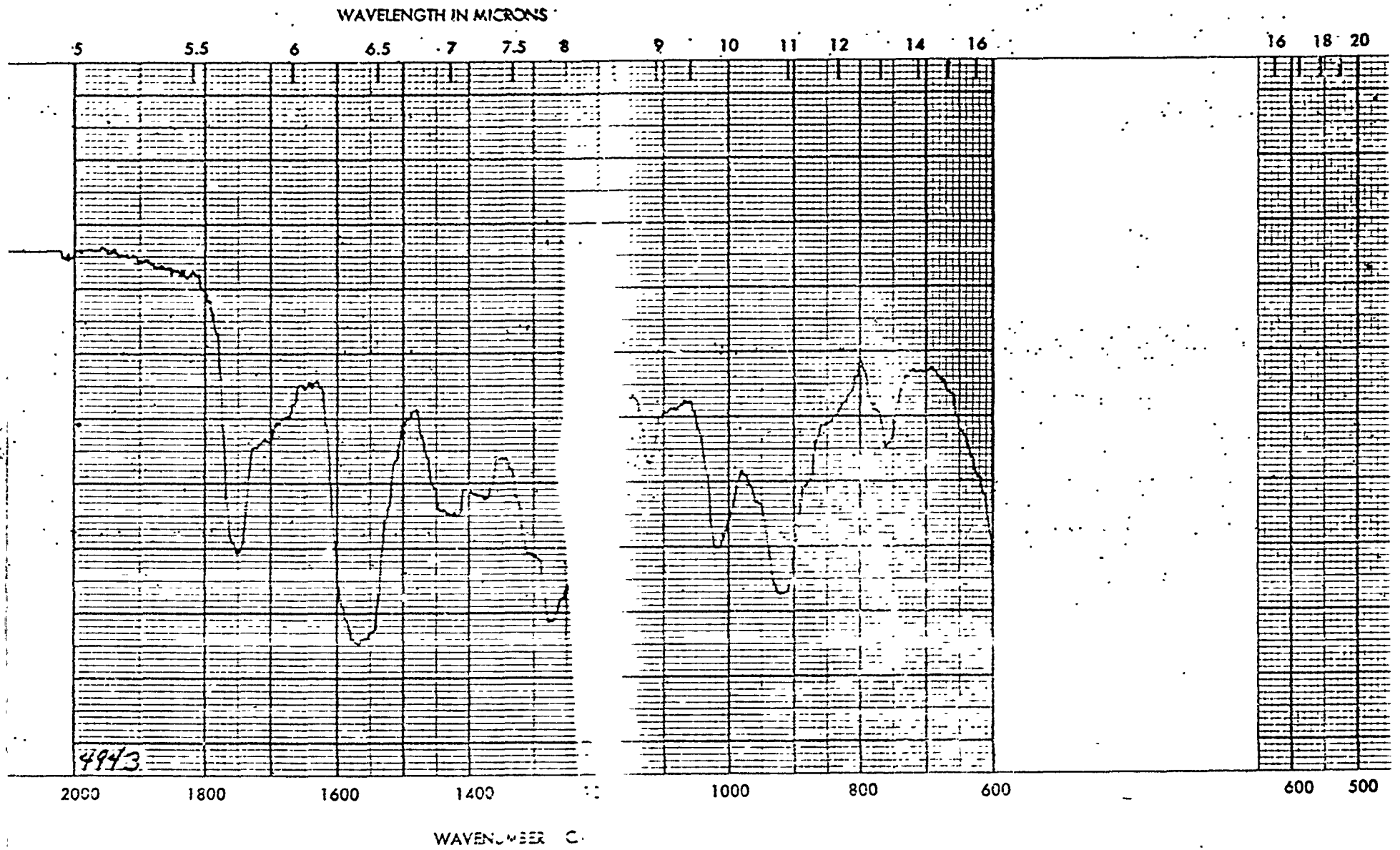


Figure C-4D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

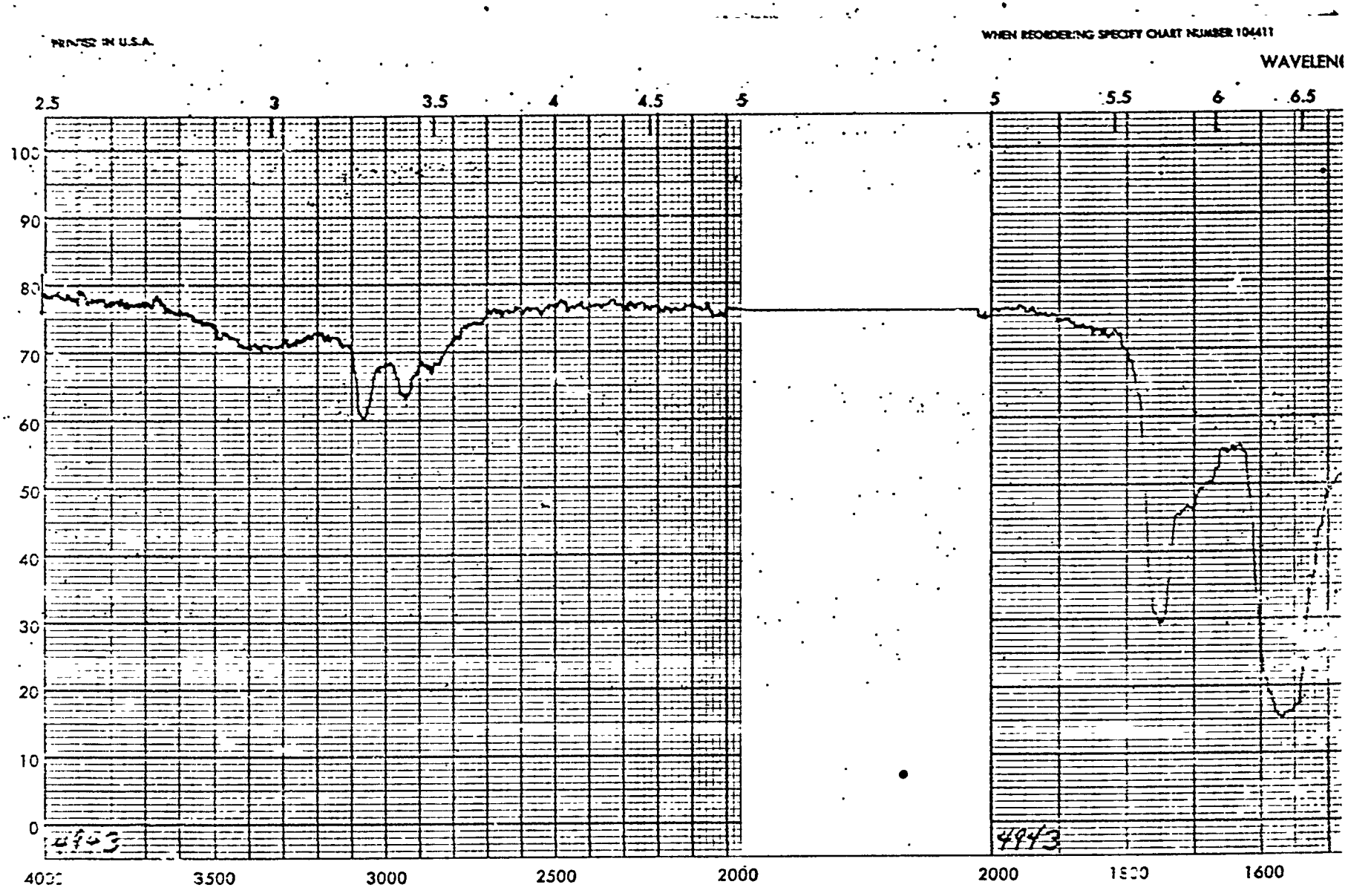


Figure C-4D (Continued). IR Spectrum of RDX Dewater Fraction No. 6

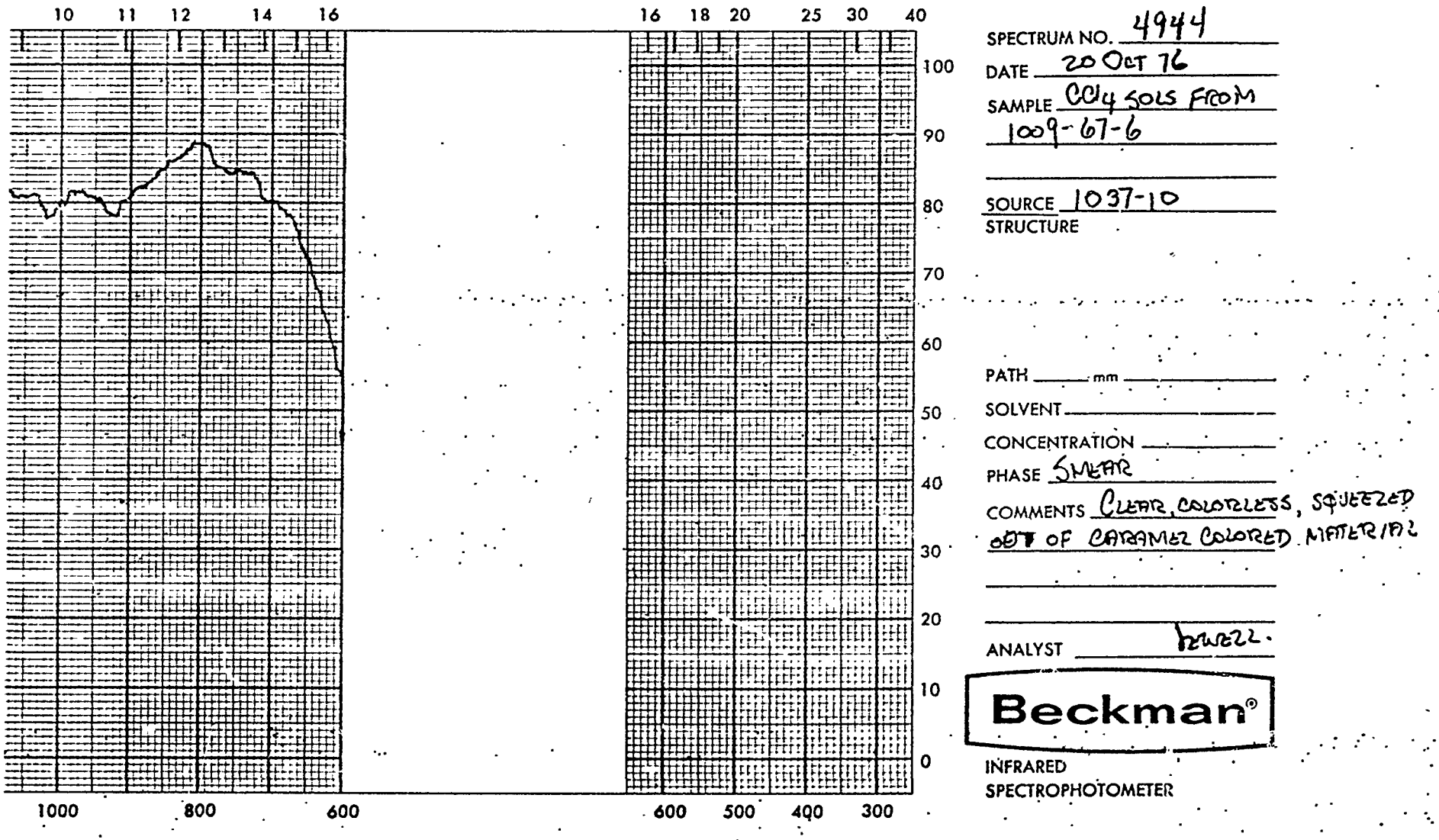


Figure C-5D. IR Spectrum of RDX Dewater Fraction No. 6

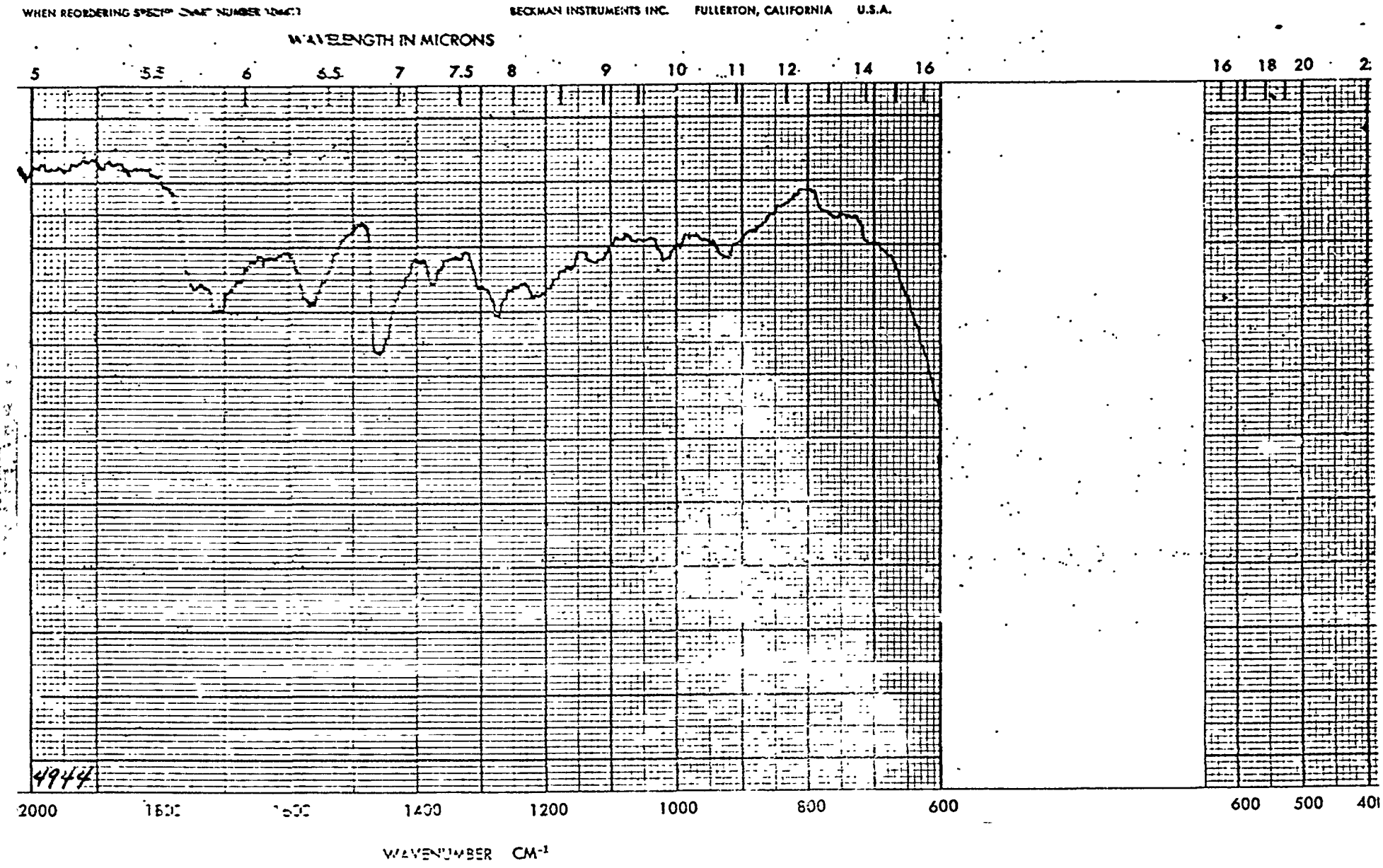


Figure C-5D (Continued). IR Spectrum of RDX Dewater Fraction No. 5

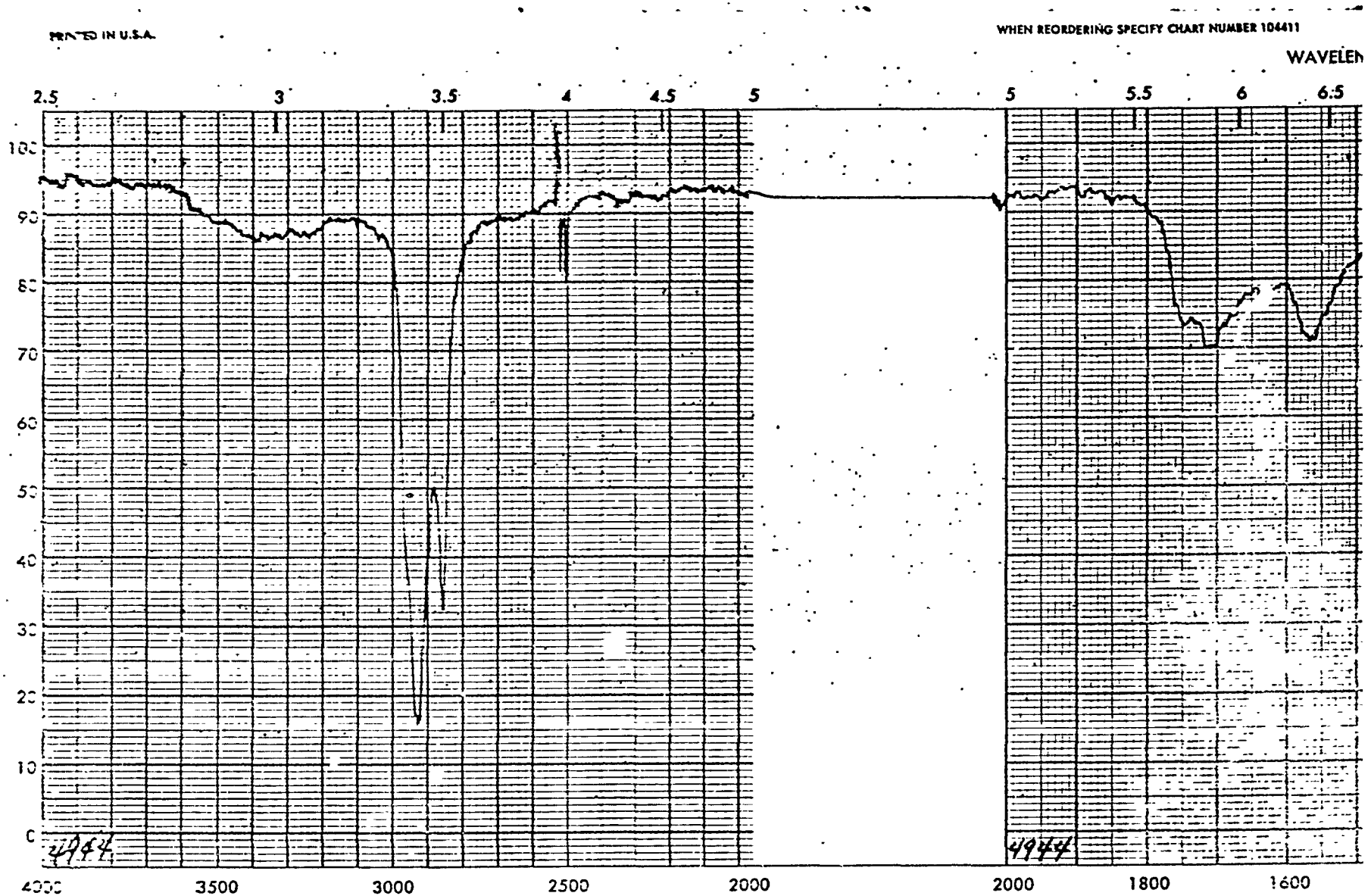
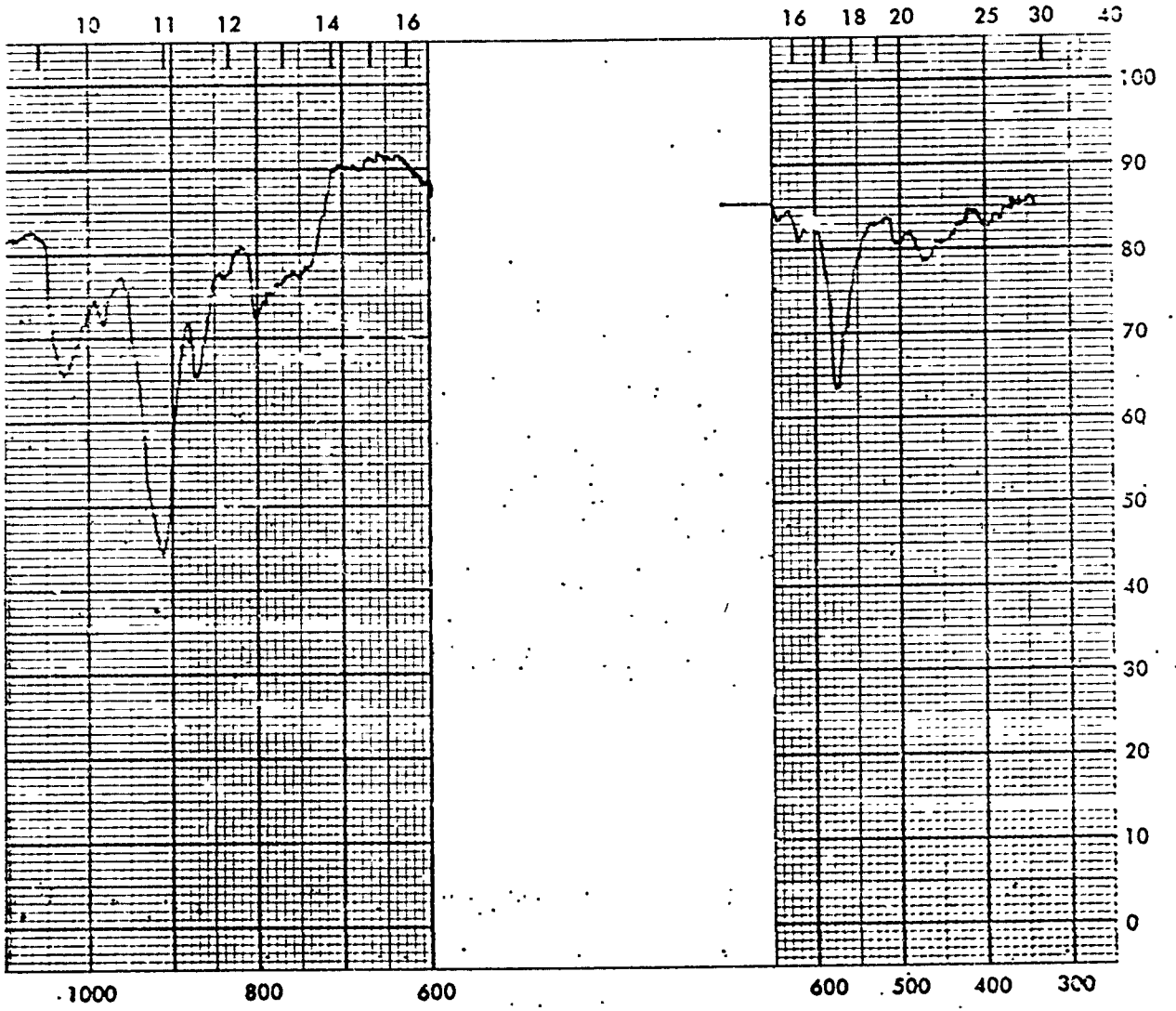


Figure C-5D (Continued). IR Spectrum of RDX Dewatev Fraction No. 6

ENTS INC. FULLERTON, CALIFORNIA U.S.A.



SPECTRUM NO. 4967

DATE 5 Nov 76

SAMPLE WHITE SOLID FROM #7
$CHCl_3$ SOL - CCl_4 INSOL
SLIGHTLY SOL IN ACETONE

SOURCE ORSTINGHAM 1009-67-7

STRUCTURE

PATH ____ mm

SOLVENT

CONCENTRATION

PHASE KBr

COMMENTS YELLOW COLOR RINSED OUT W ACETONE. SOME OF THIS SAMPLE IN BEARER 7 $CHCl_3$ B.

ANALYST Powell.

Beckman®

INFRARED SPECTROPHOTOMETER

Figure C-6D. IR Spectrum of RDX Dewater Fraction No. 7

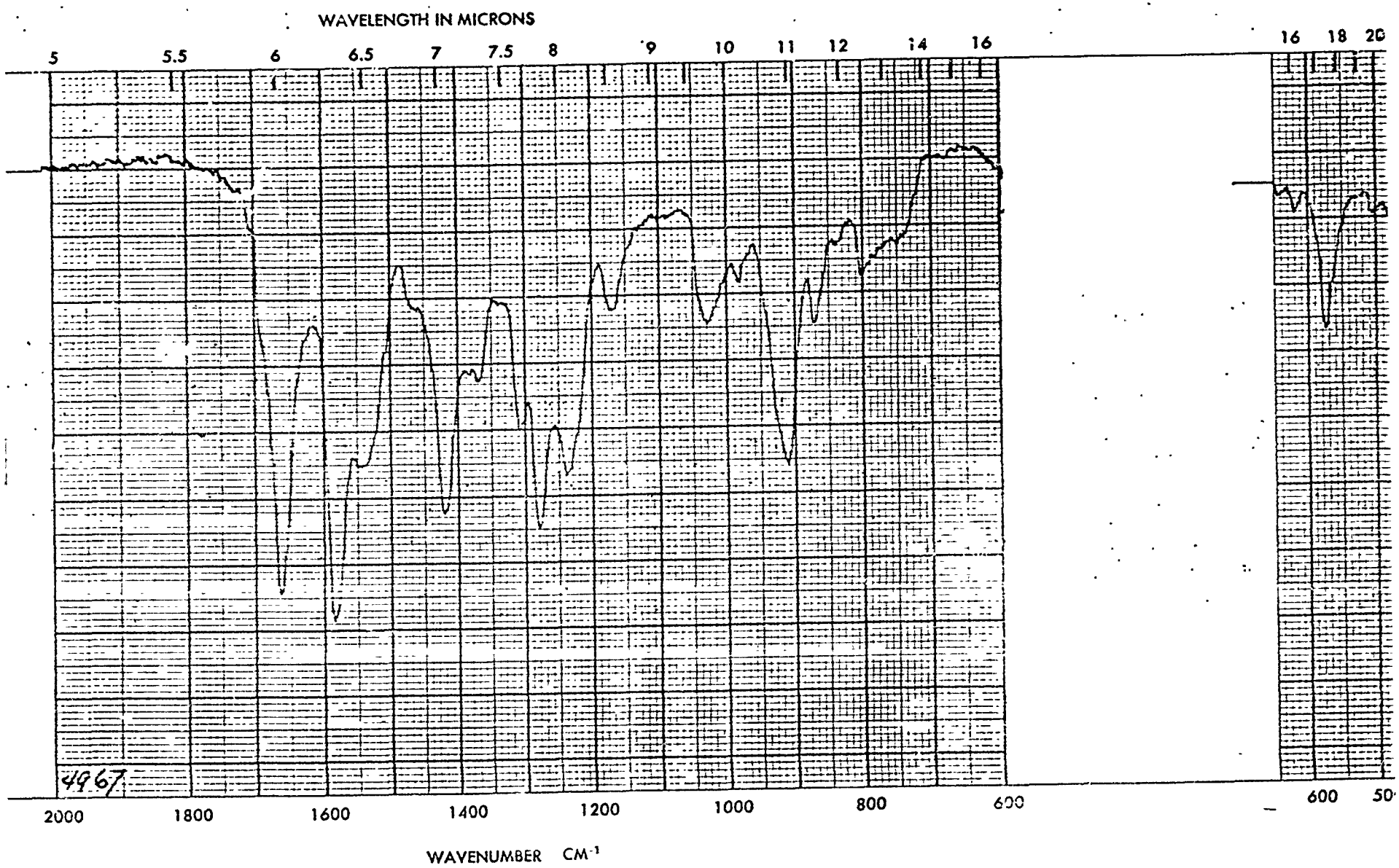


Figure C-6D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

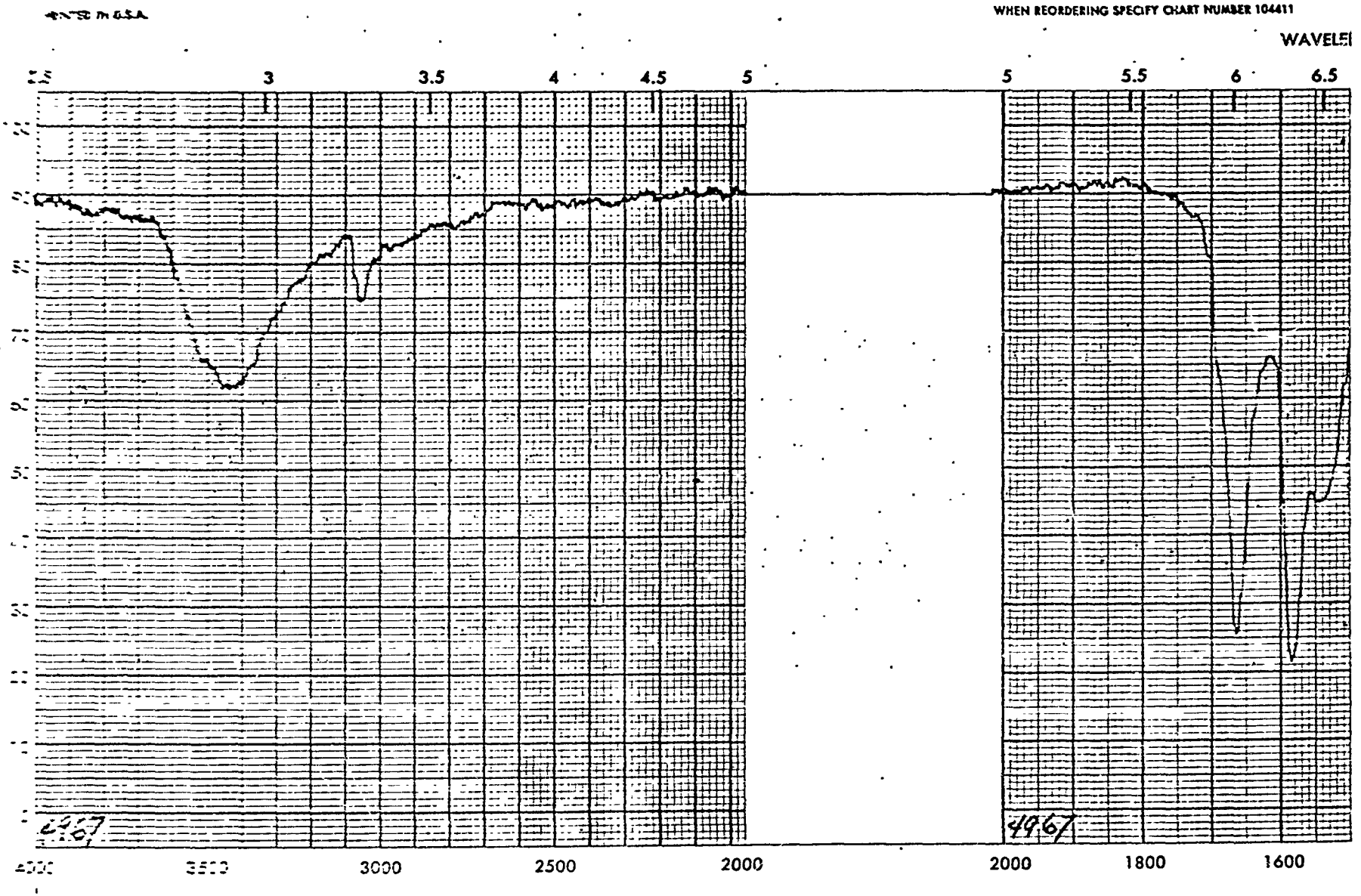


Figure C-6D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

ENTS INC. FULLERTON, CALIFORNIA U.S.A.

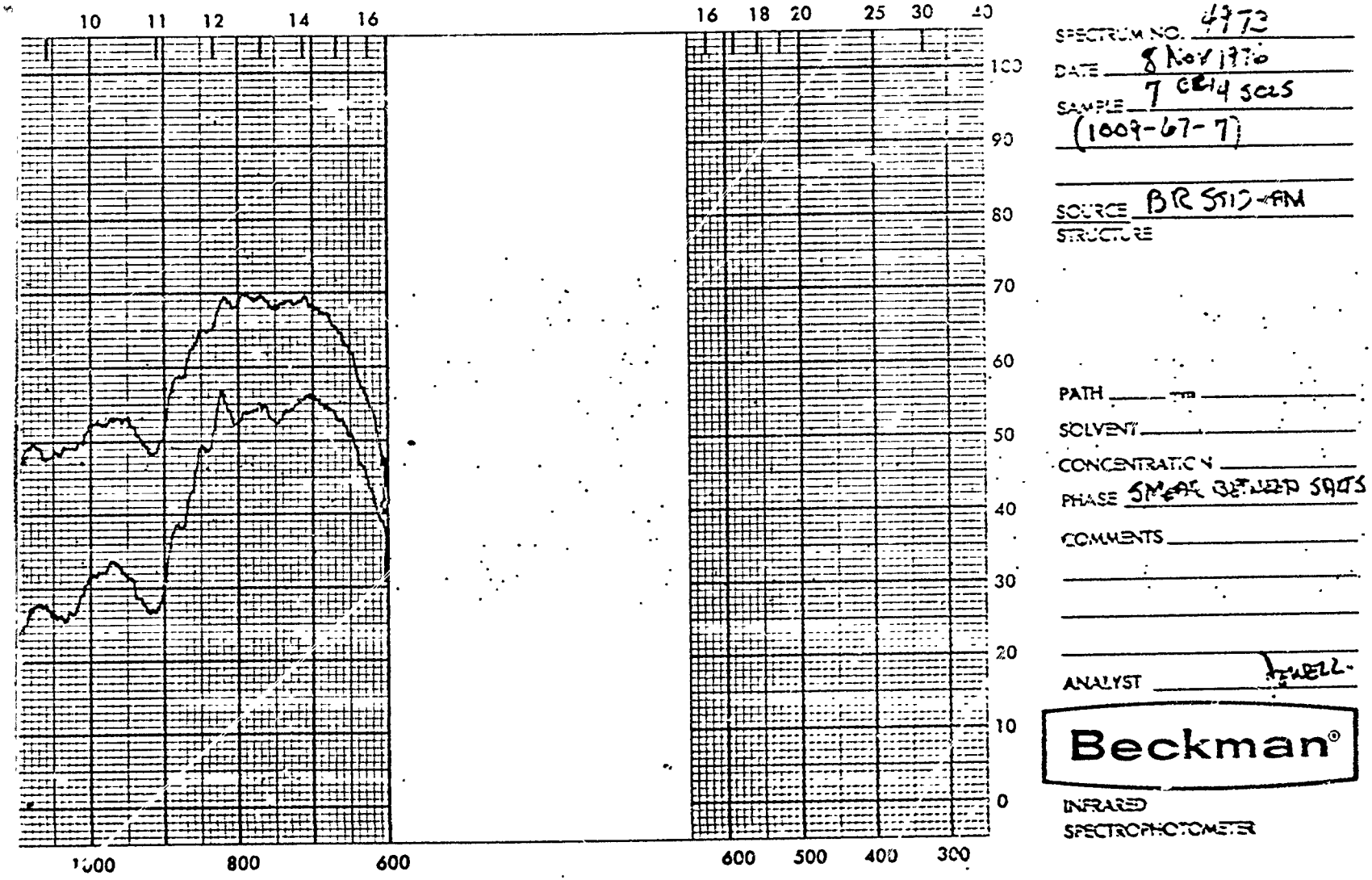


Figure C-7D. IR Spectrum of RDX Dewater Fraction No. 7

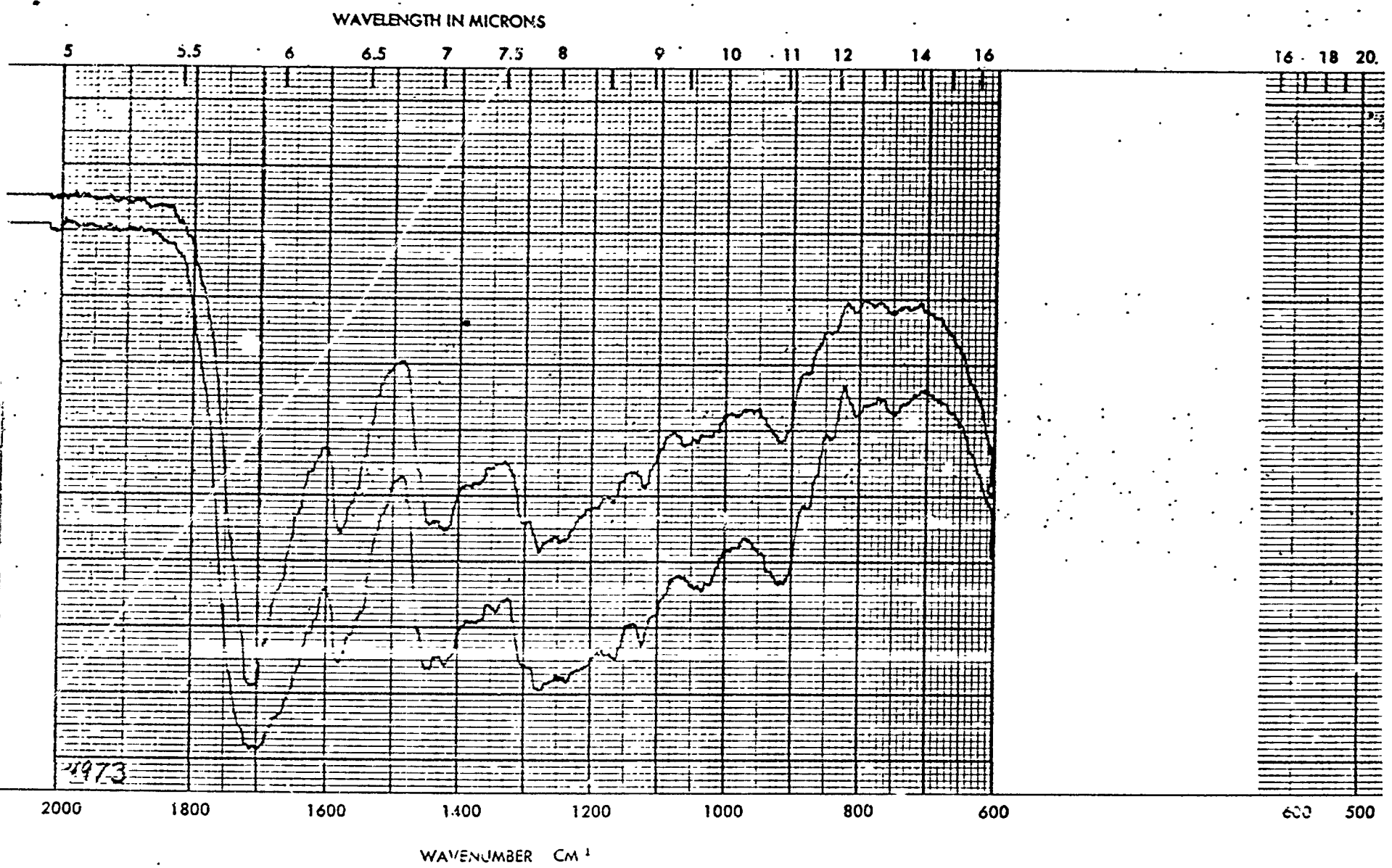


Figure C-7D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

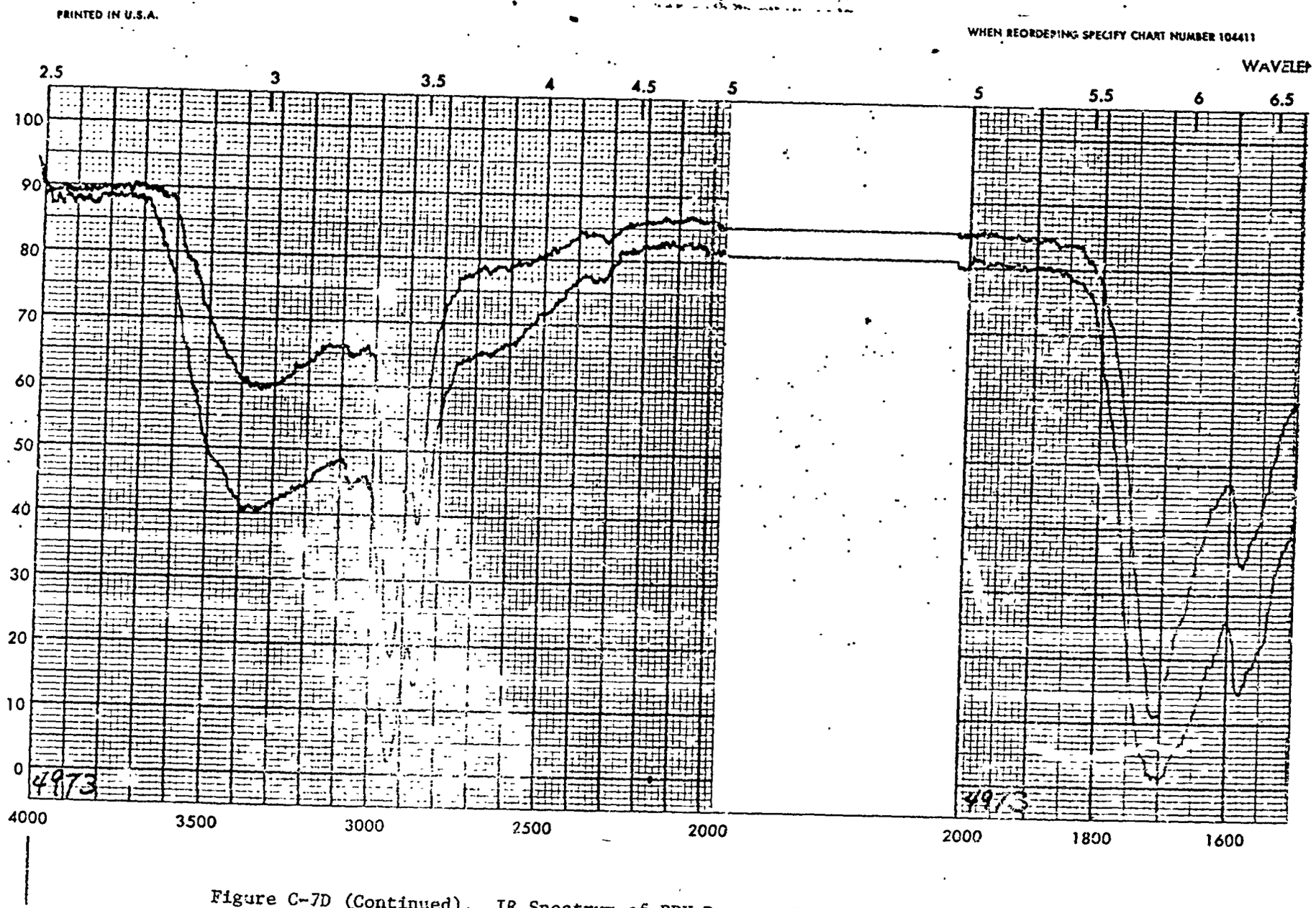


Figure C-7D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

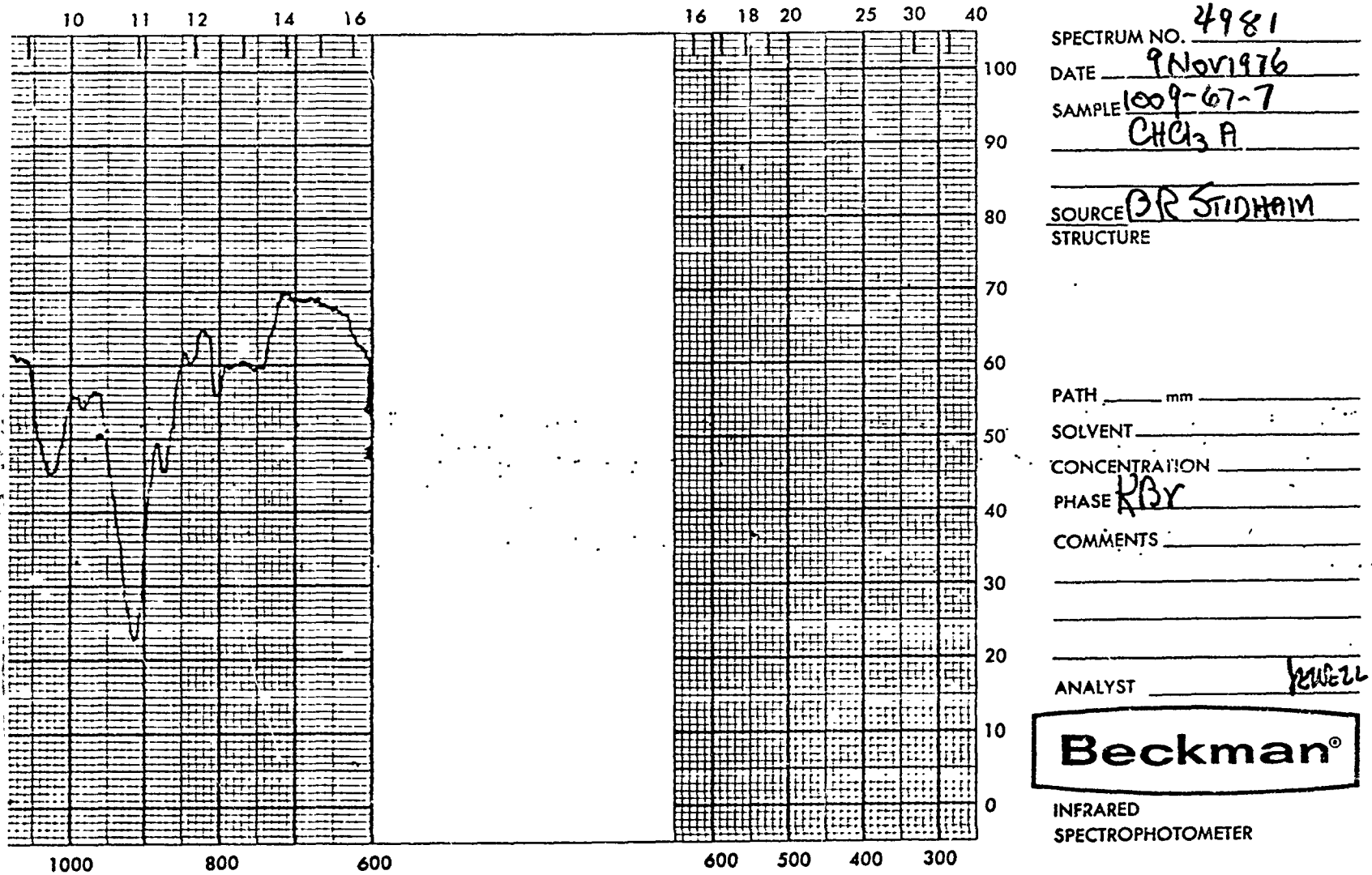


Figure C-8D. IR Spectrum of RDX Dewater Fraction No. 7

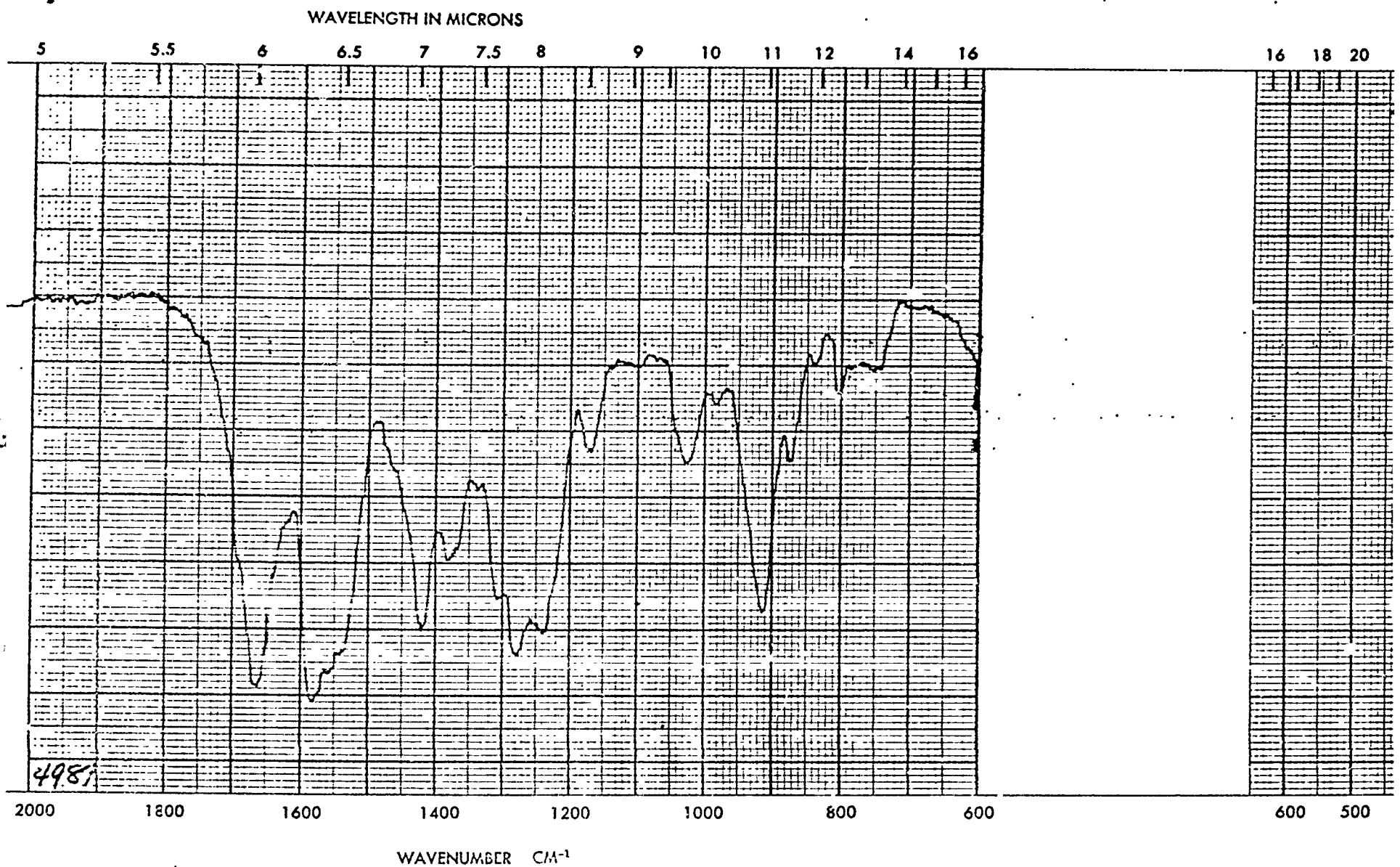


Figure C-8D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

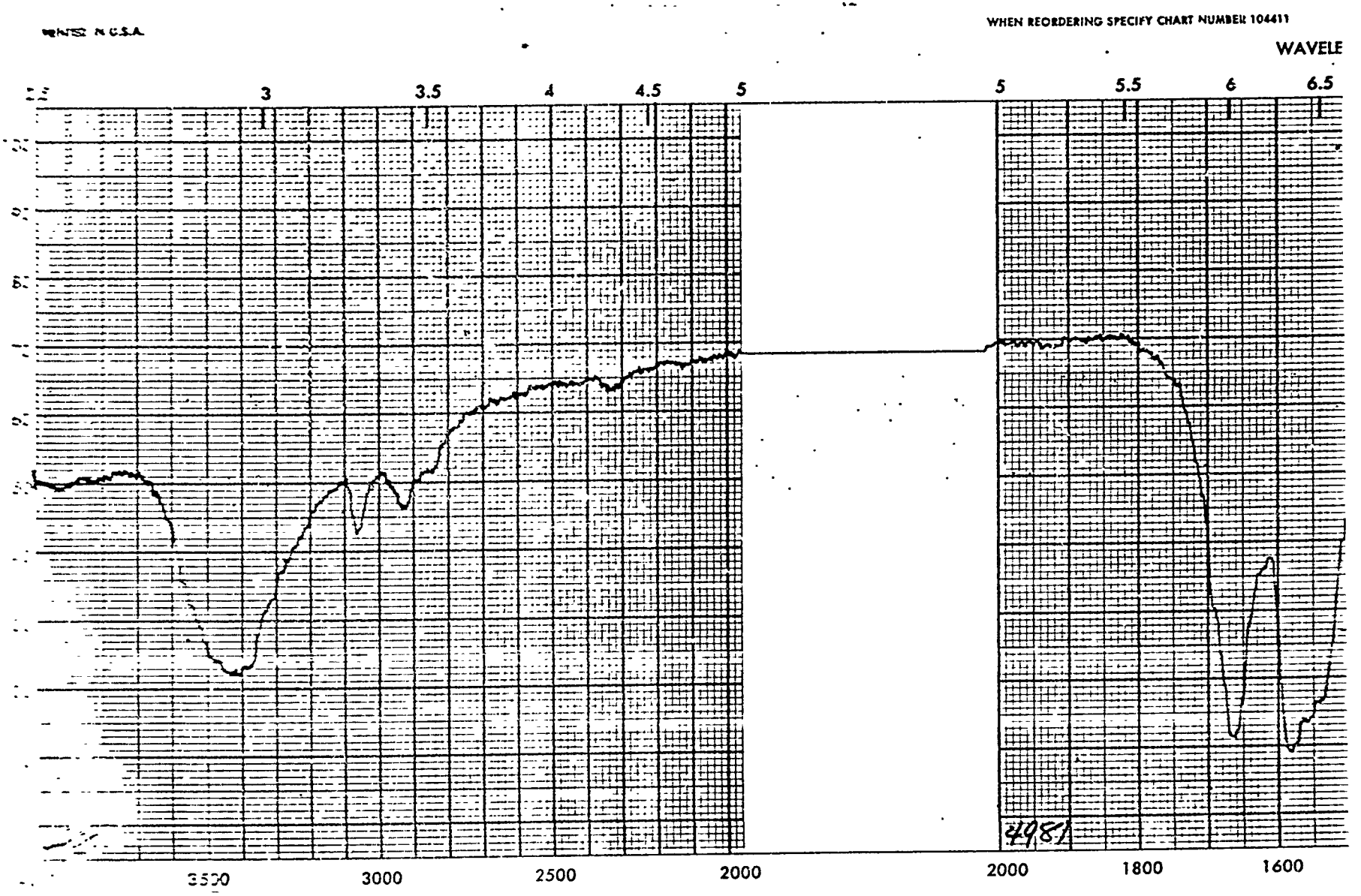


Figure C-8D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

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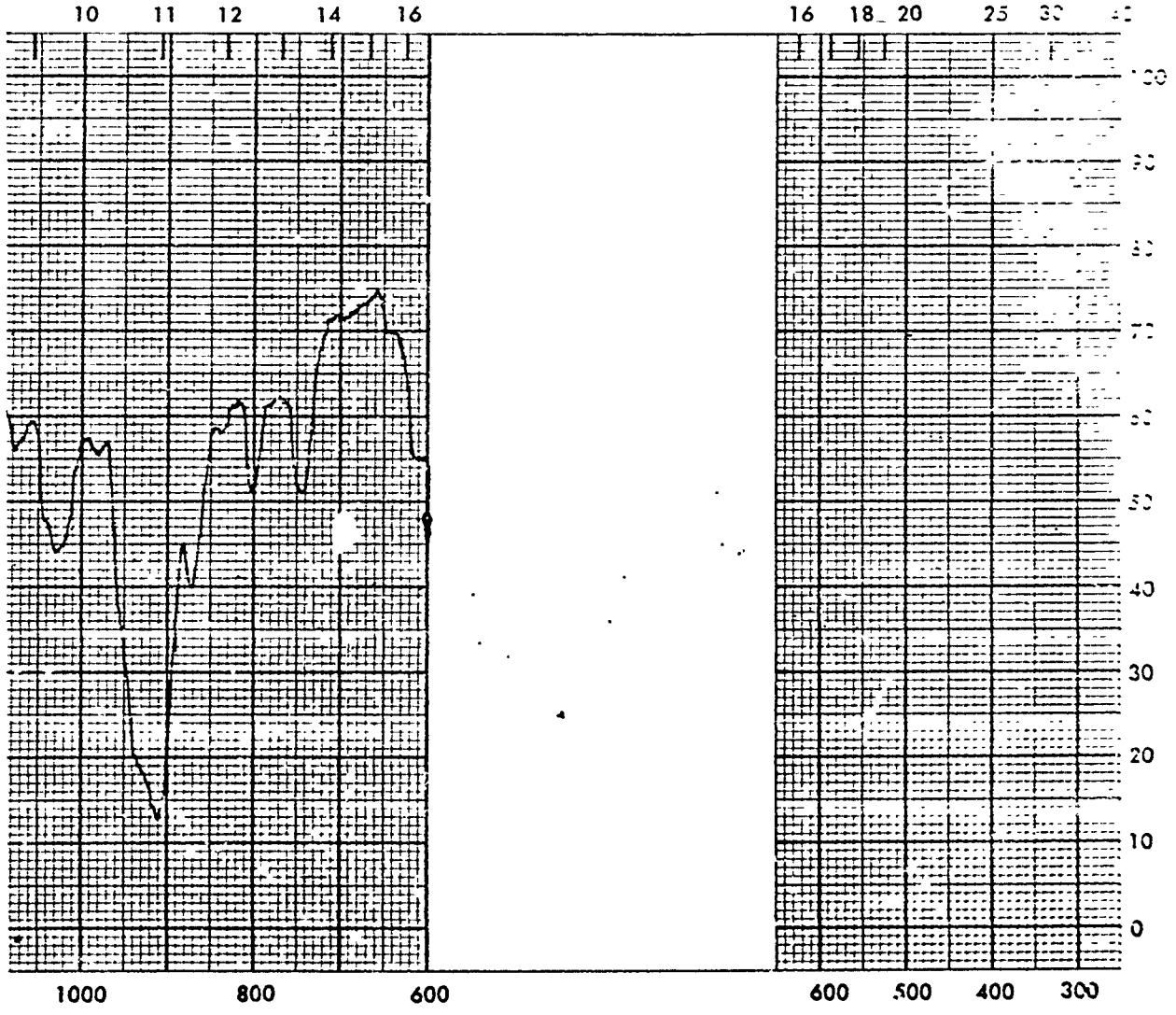


SPECTRUM NO. 4983
DATE 9 Nov 1976
SAMPLE 1009-67-7
RESIDUE AFTER LEACHING FOR 16 WITH MIXTURE OF ACETONE & WATER
SOURCE BR STIGAM
STRUCTURE

PATH ____ mm
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS

ANALYST

Beckman
INFRARED
SPECTROPHOTOMETER

Figure C-9D. IR Spectrum of RDX Dewater Fraction No. 7

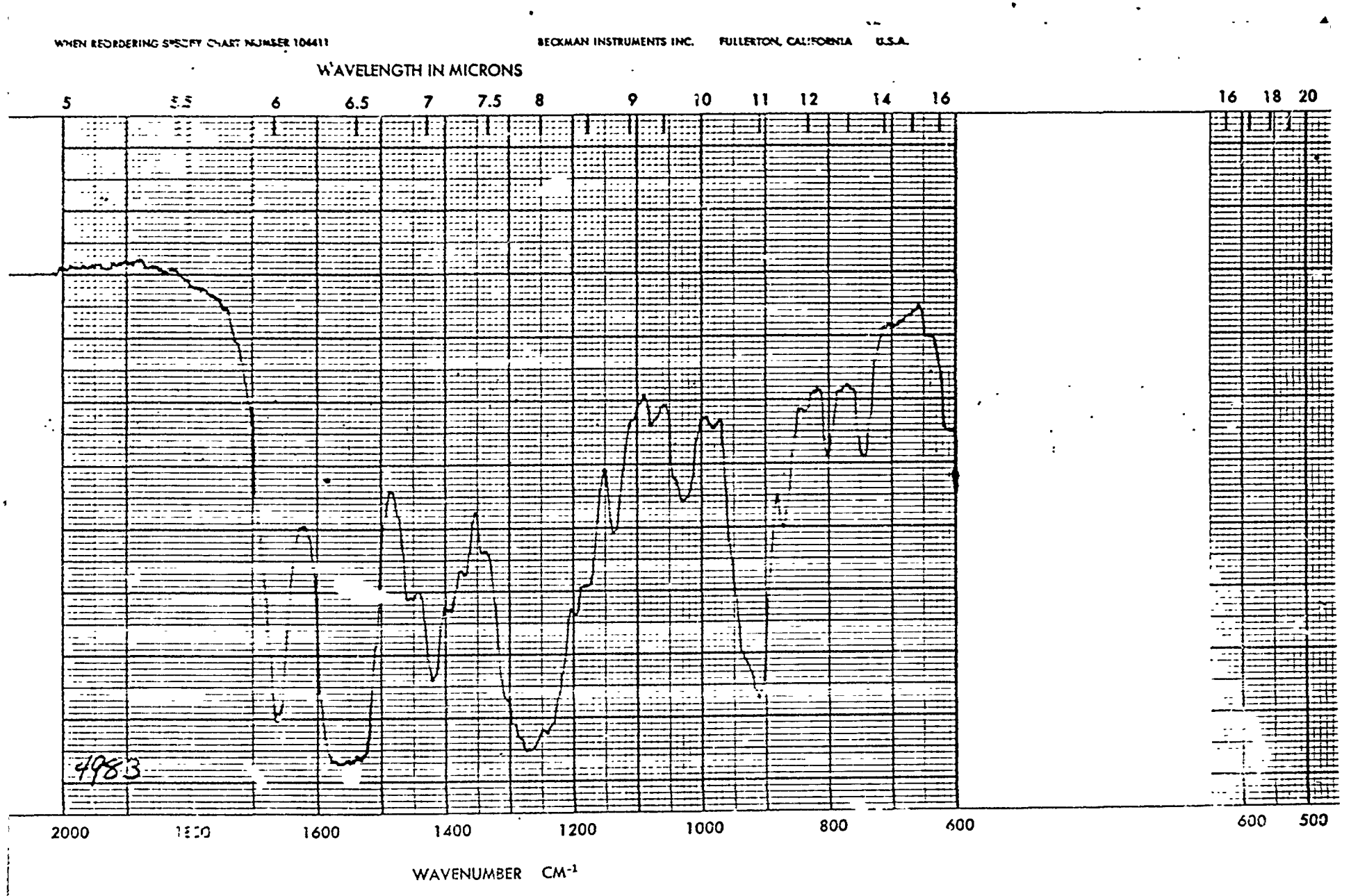


Figure C-9D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

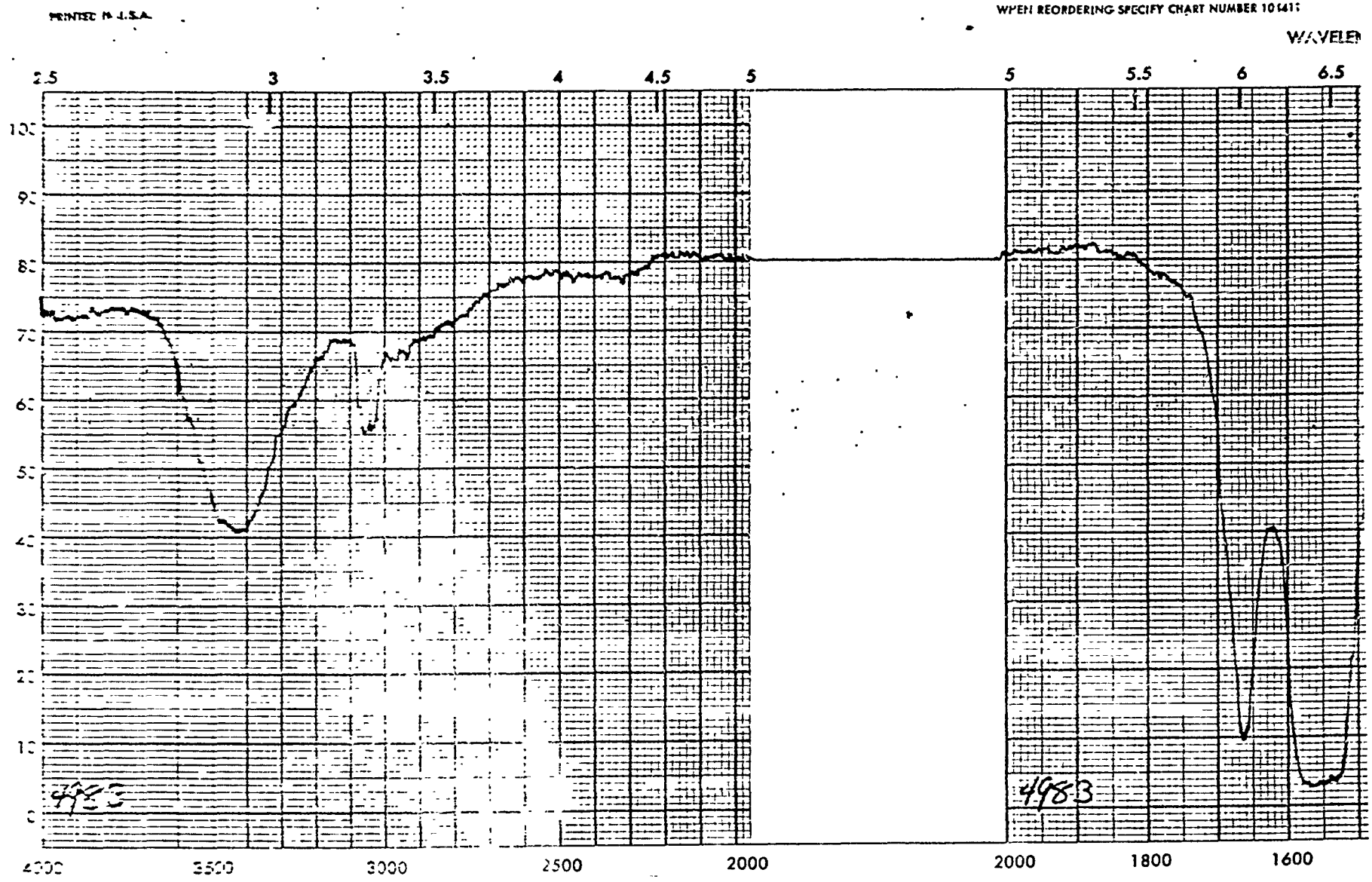


Figure C-9D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

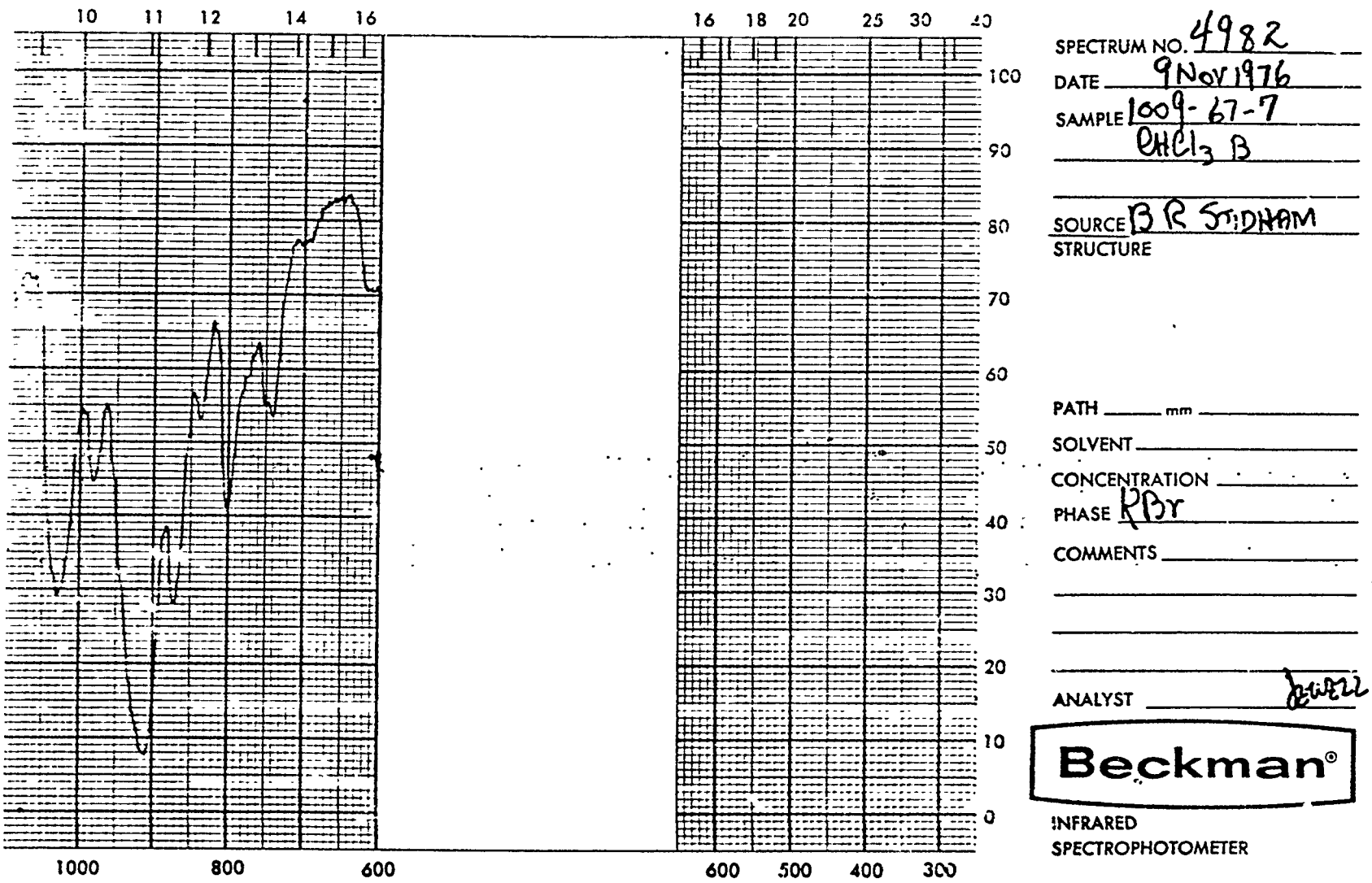


Figure C-10D. IR Spectrum of RDX Dewater Fraction No. 7

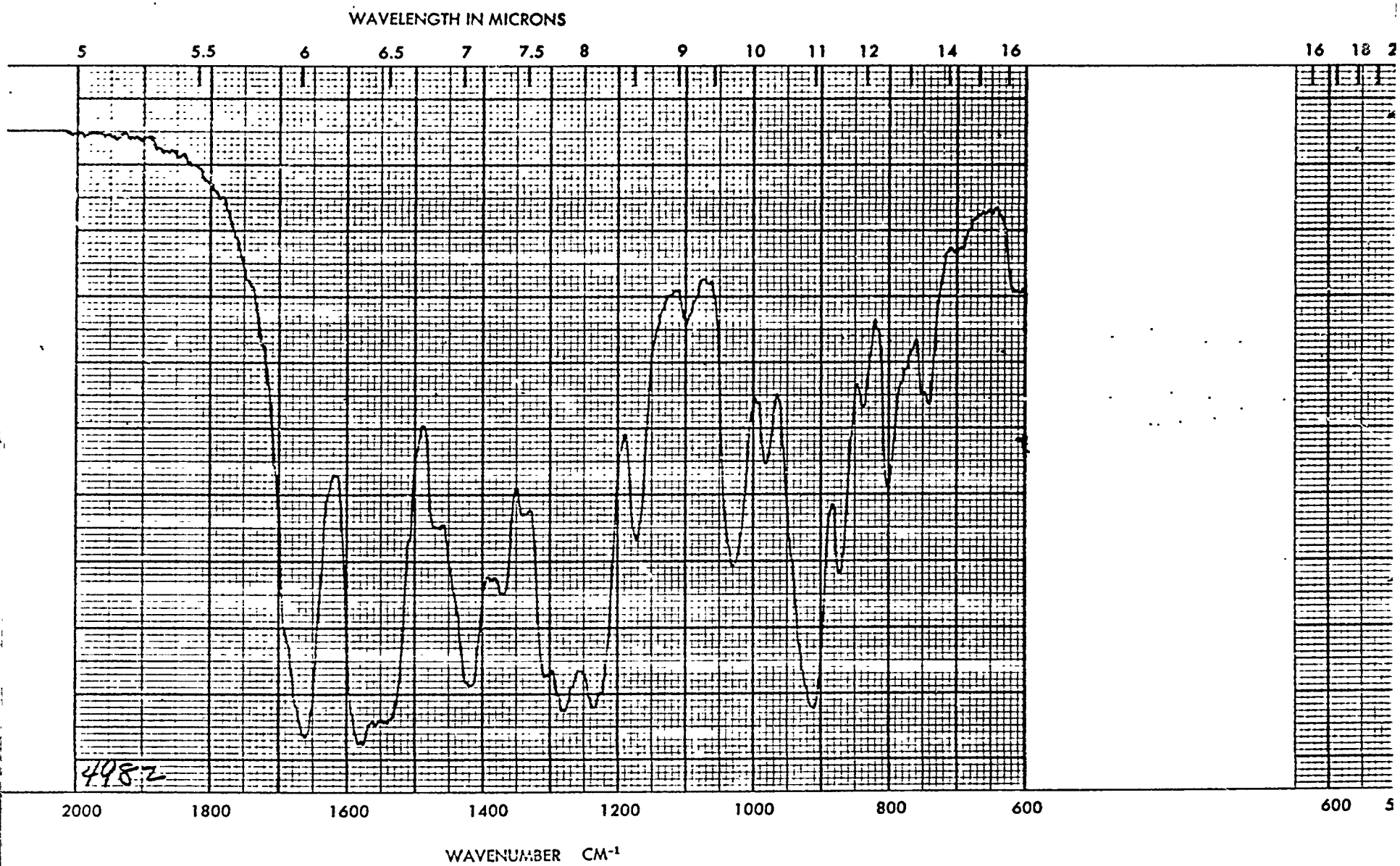


Figure C-10D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

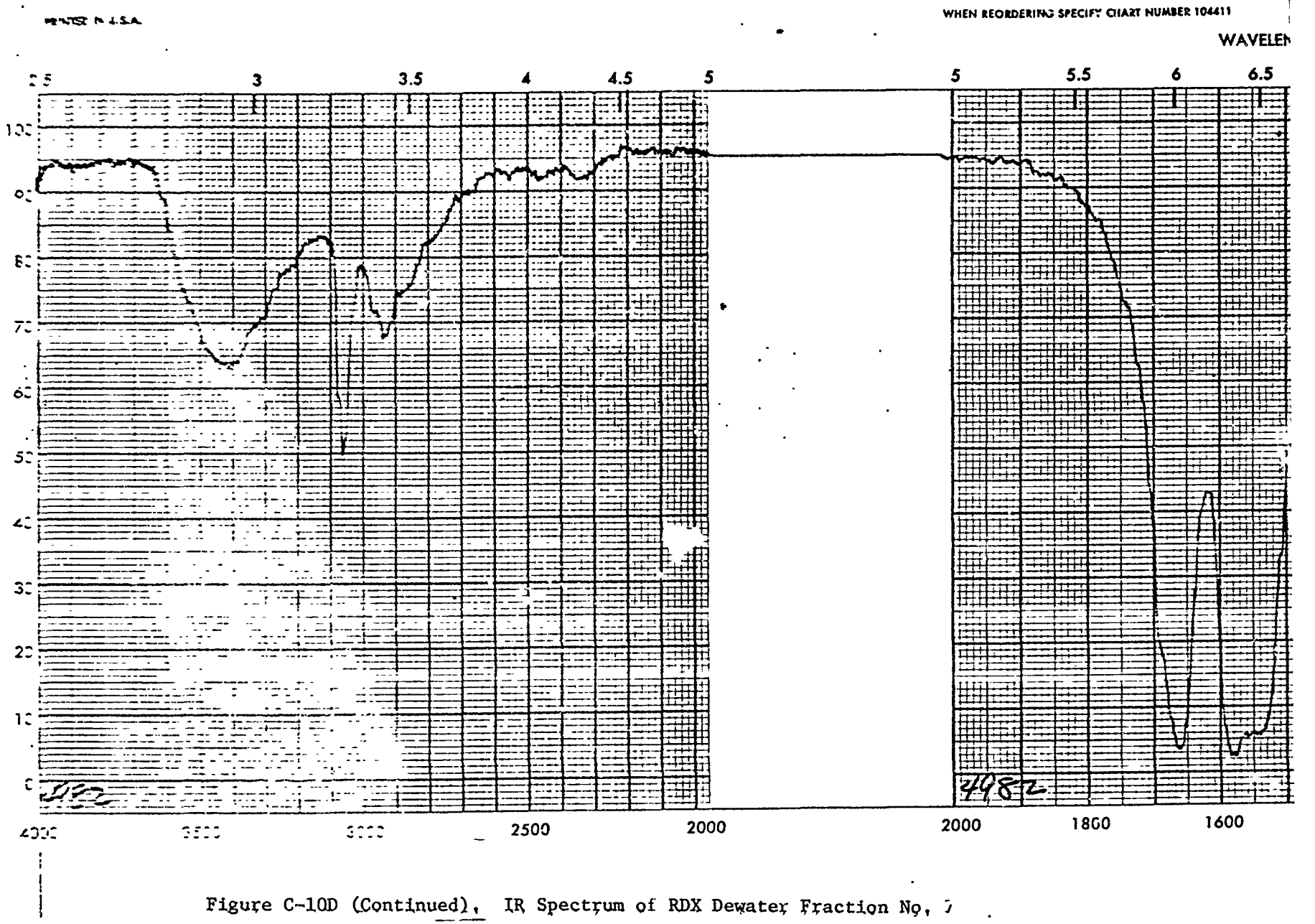


Figure C-10D (Continued), IR Spectrum of RDX Dewater Fraction No. 7

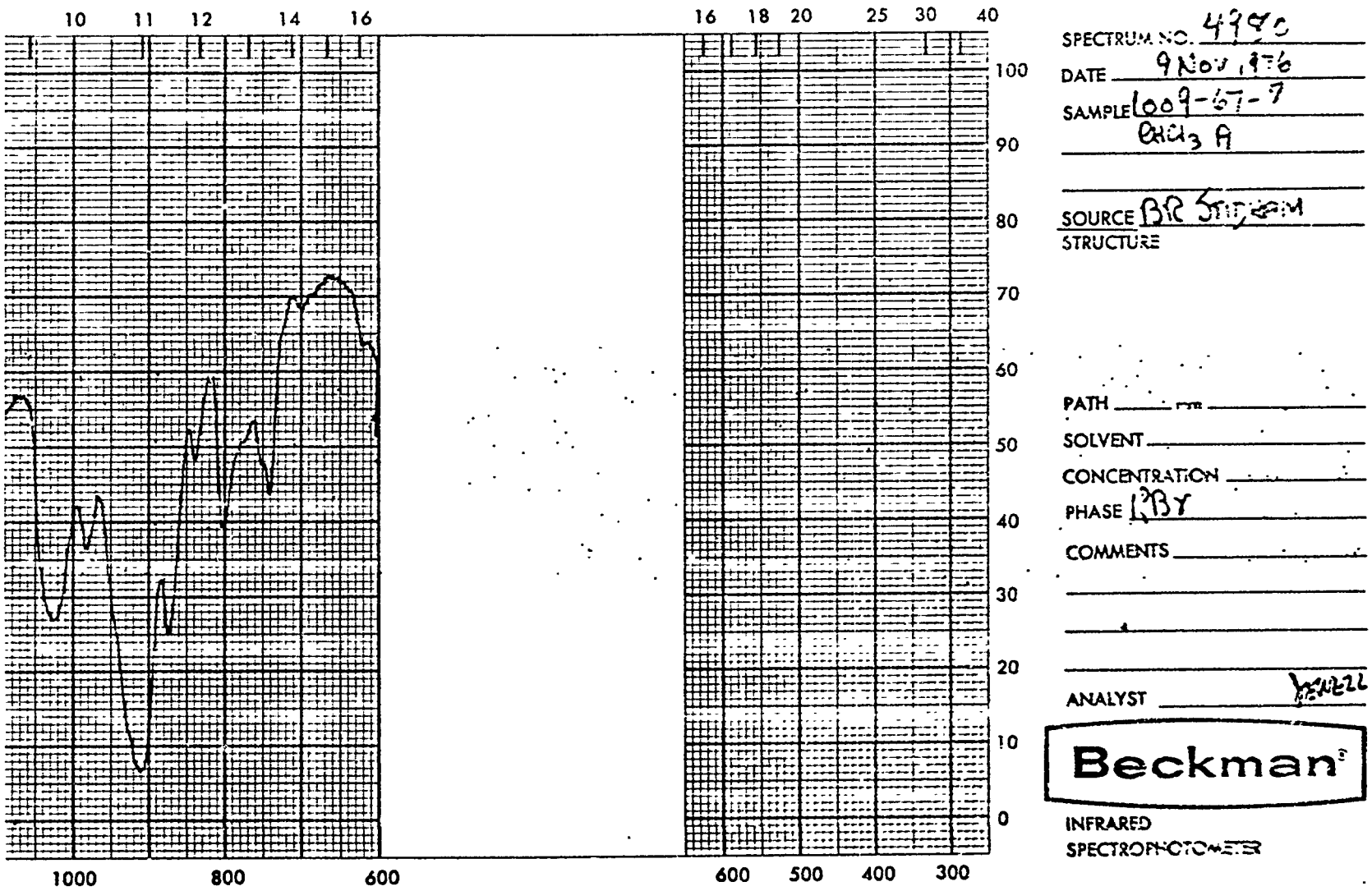


Figure C-11D. IR Spectrum of RDX Dewater Fraction No. 7

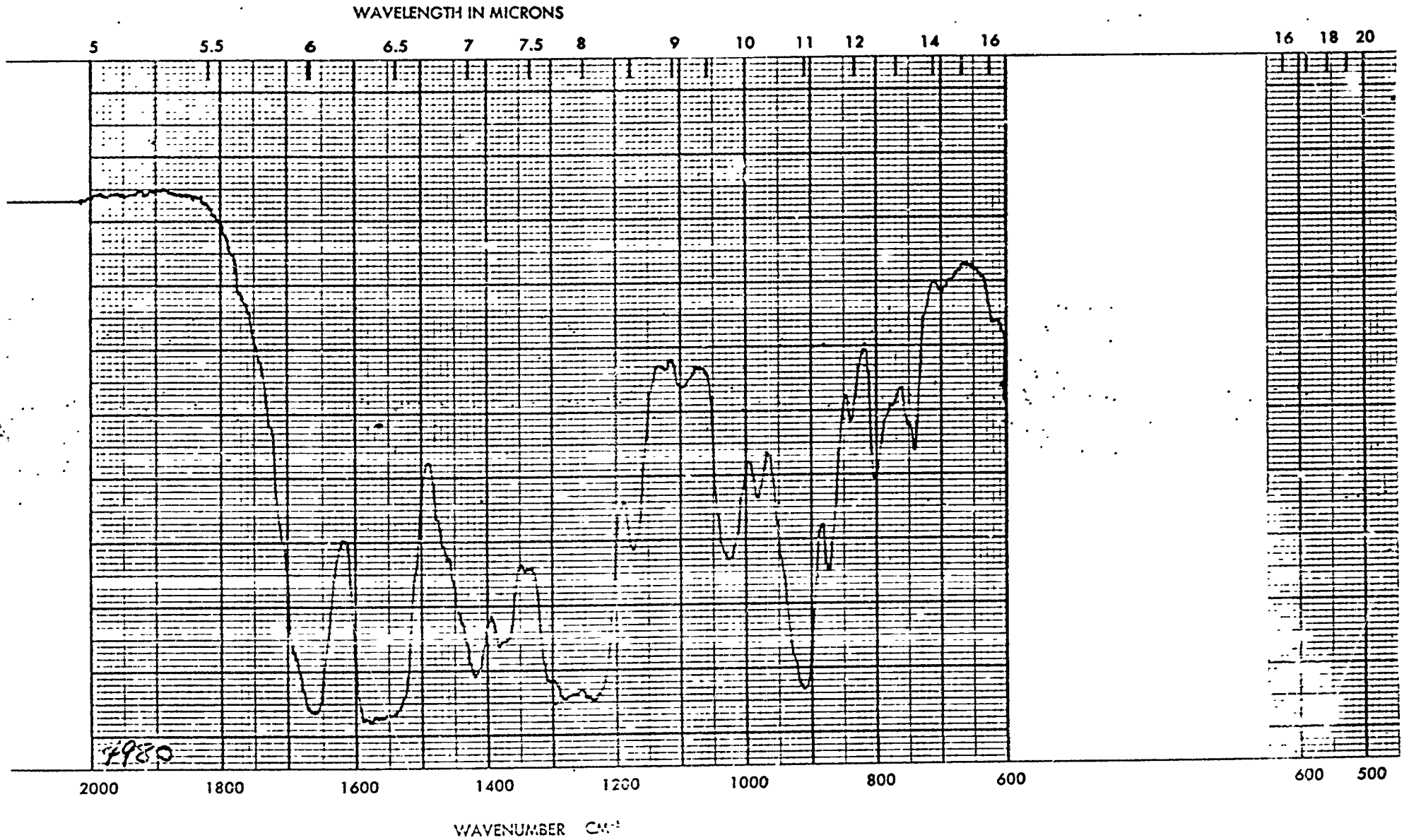


Figure C-11D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

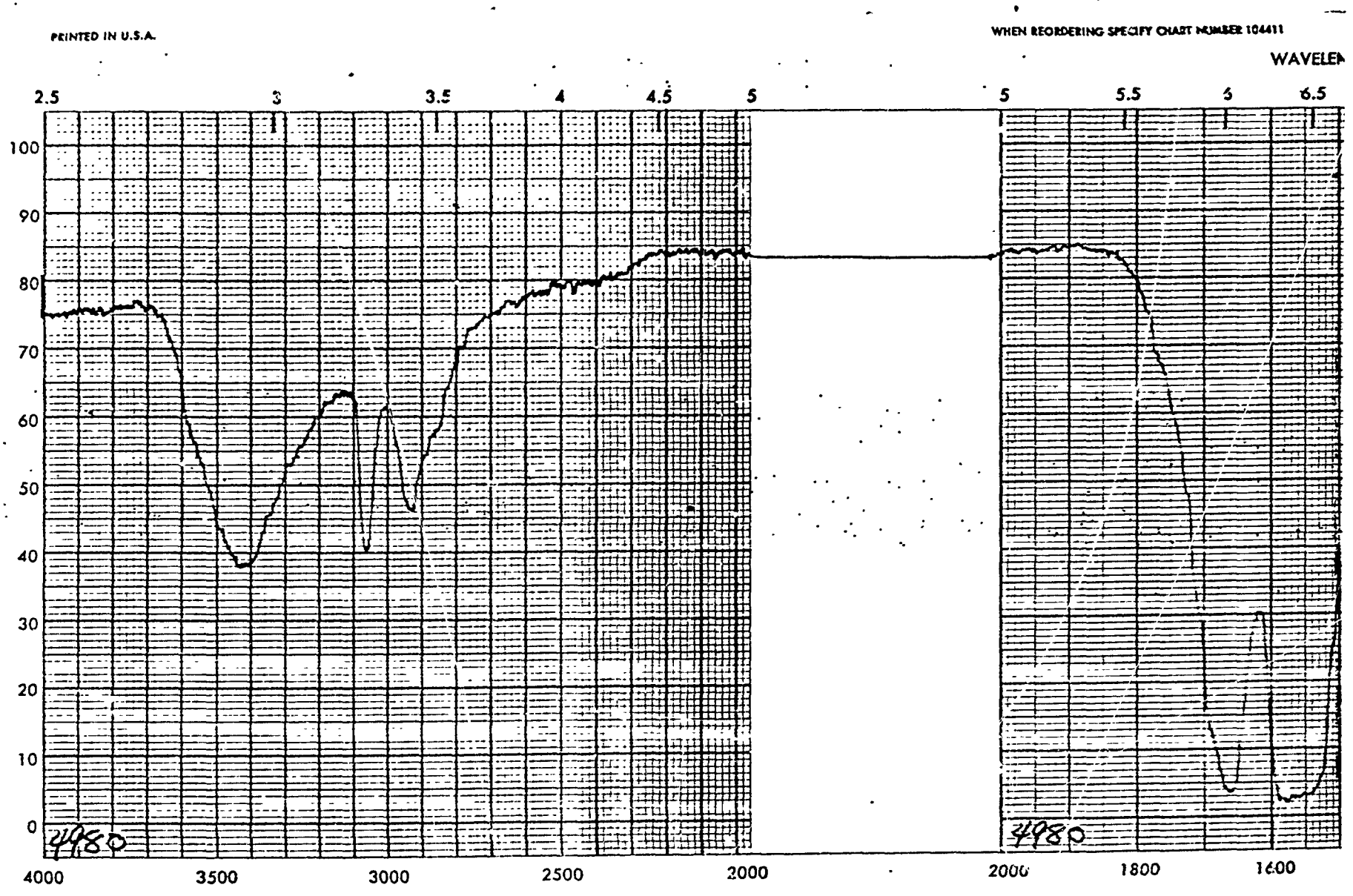


Figure C-11D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

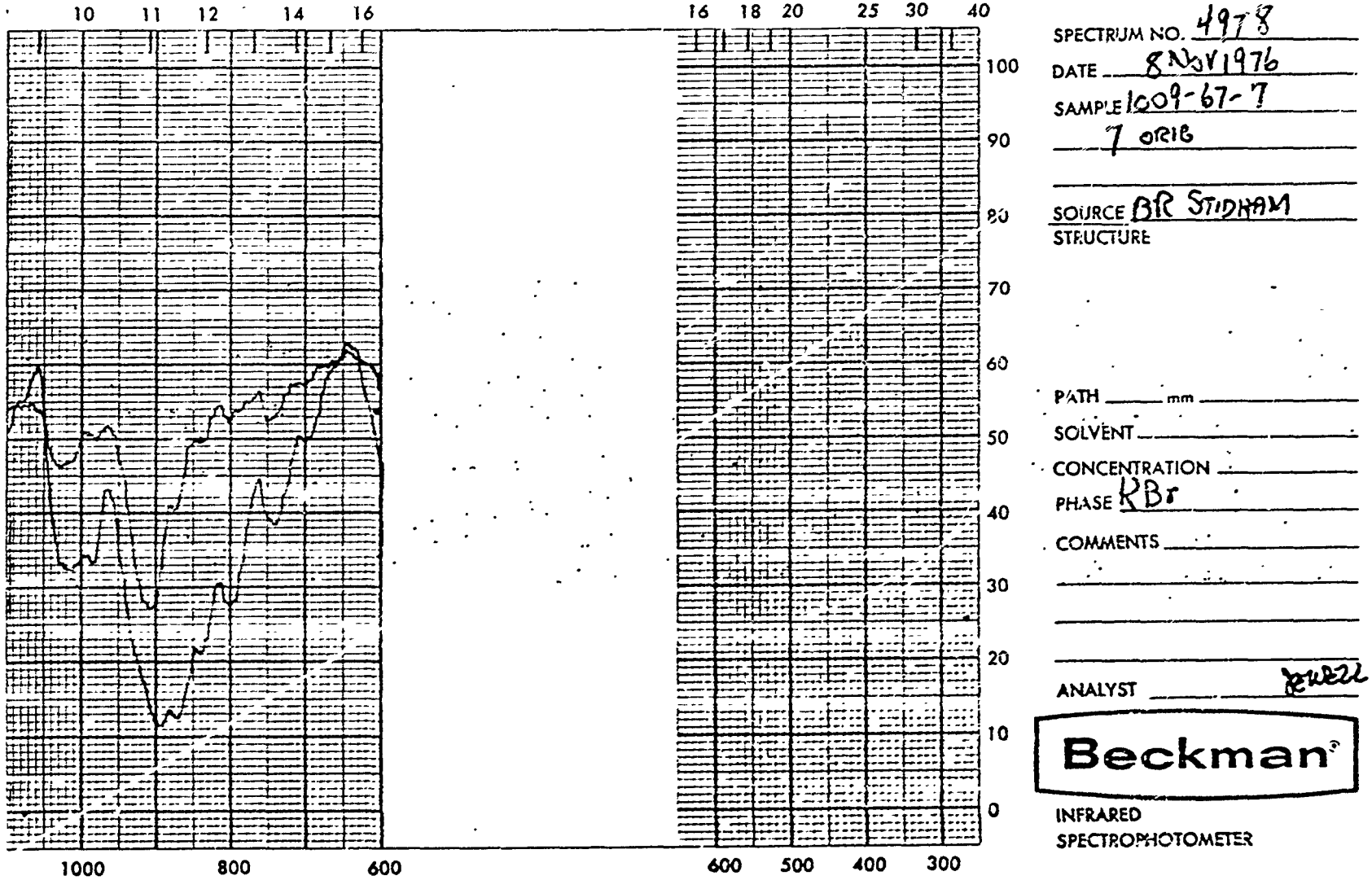


Figure C-12D. IR Spectrum of RDX Dewater Fraction No. 7

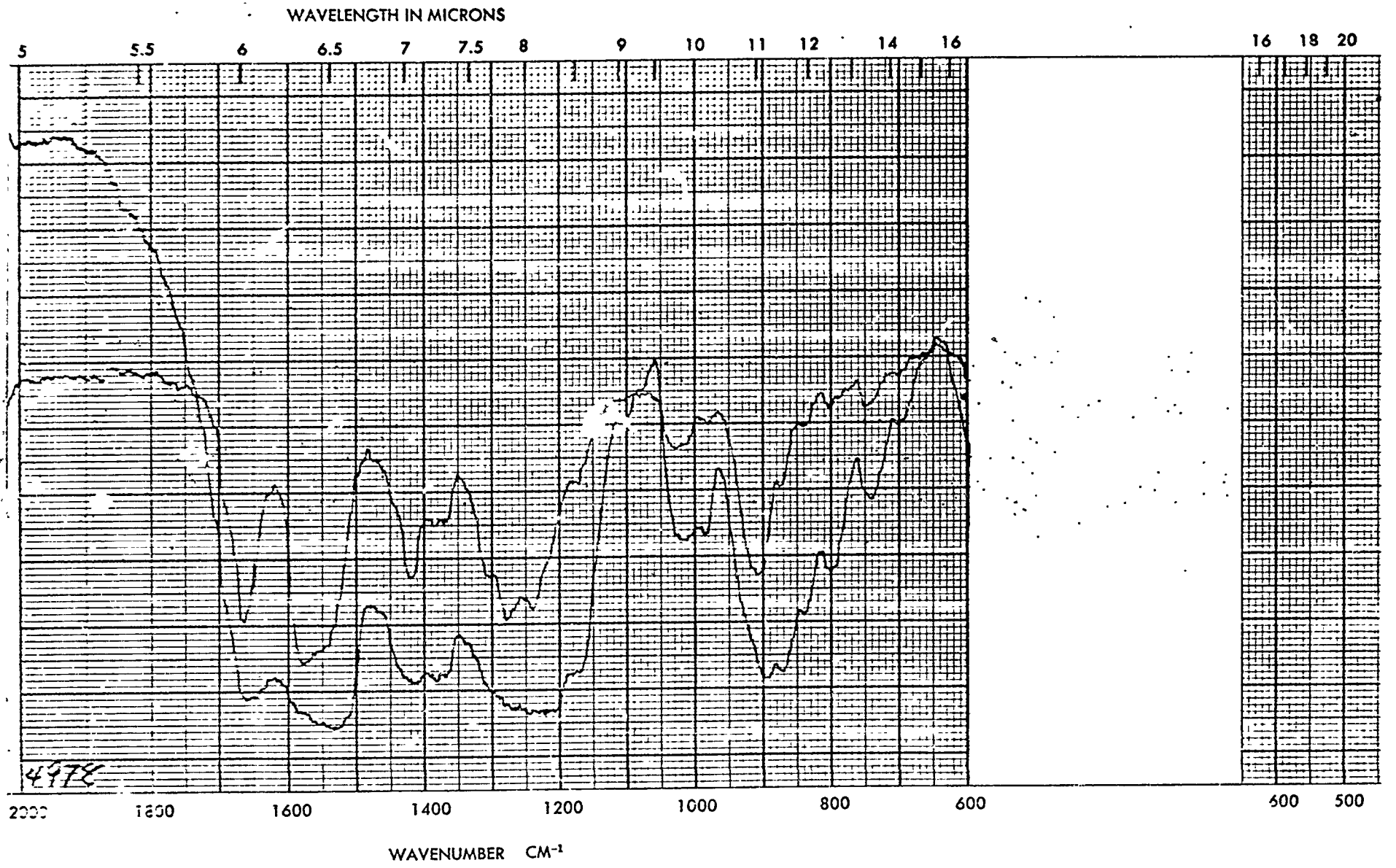


Figure C-12D (Continued). IR Spectrum of RDX Dewater Fraction No. 7

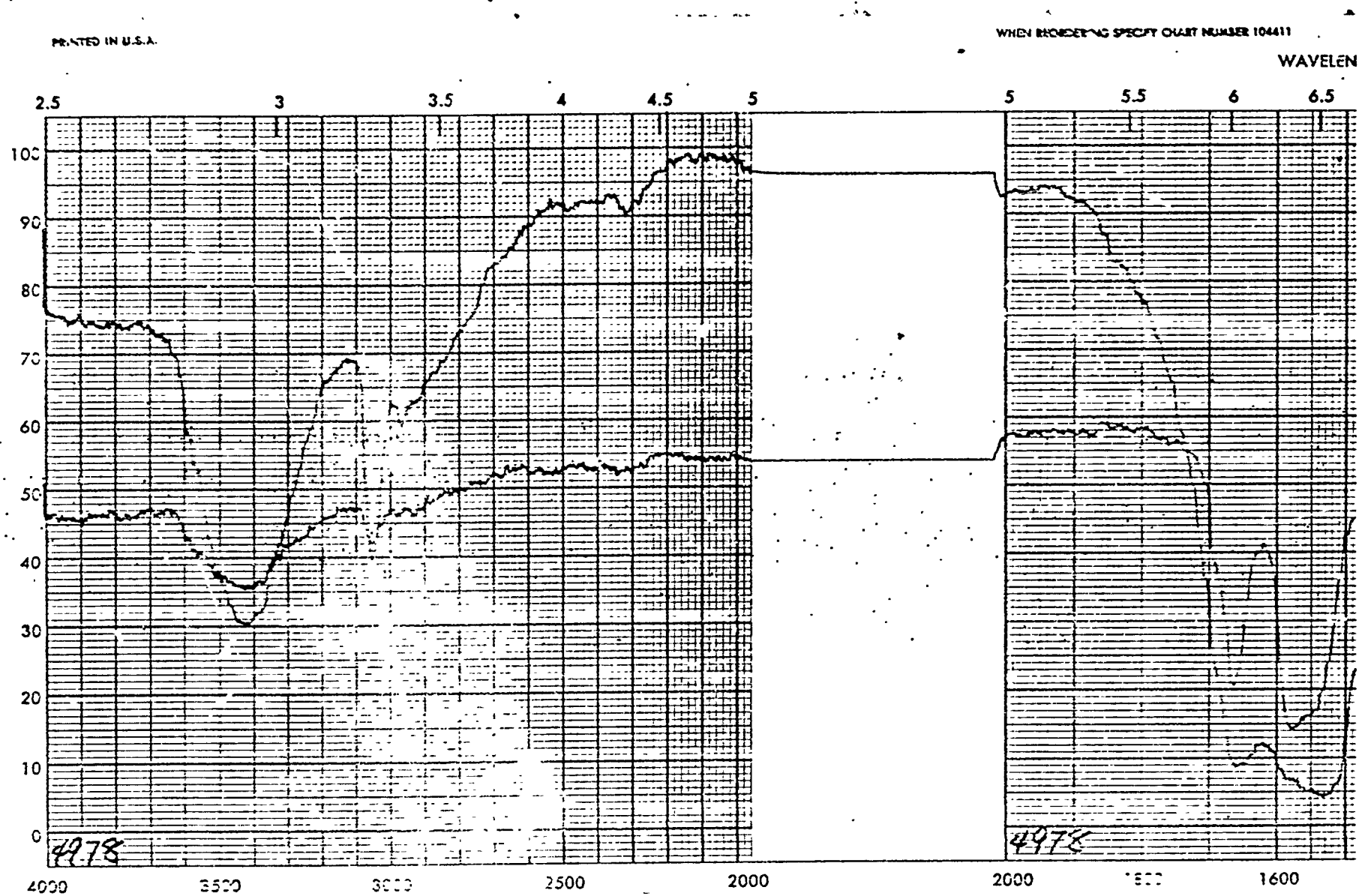
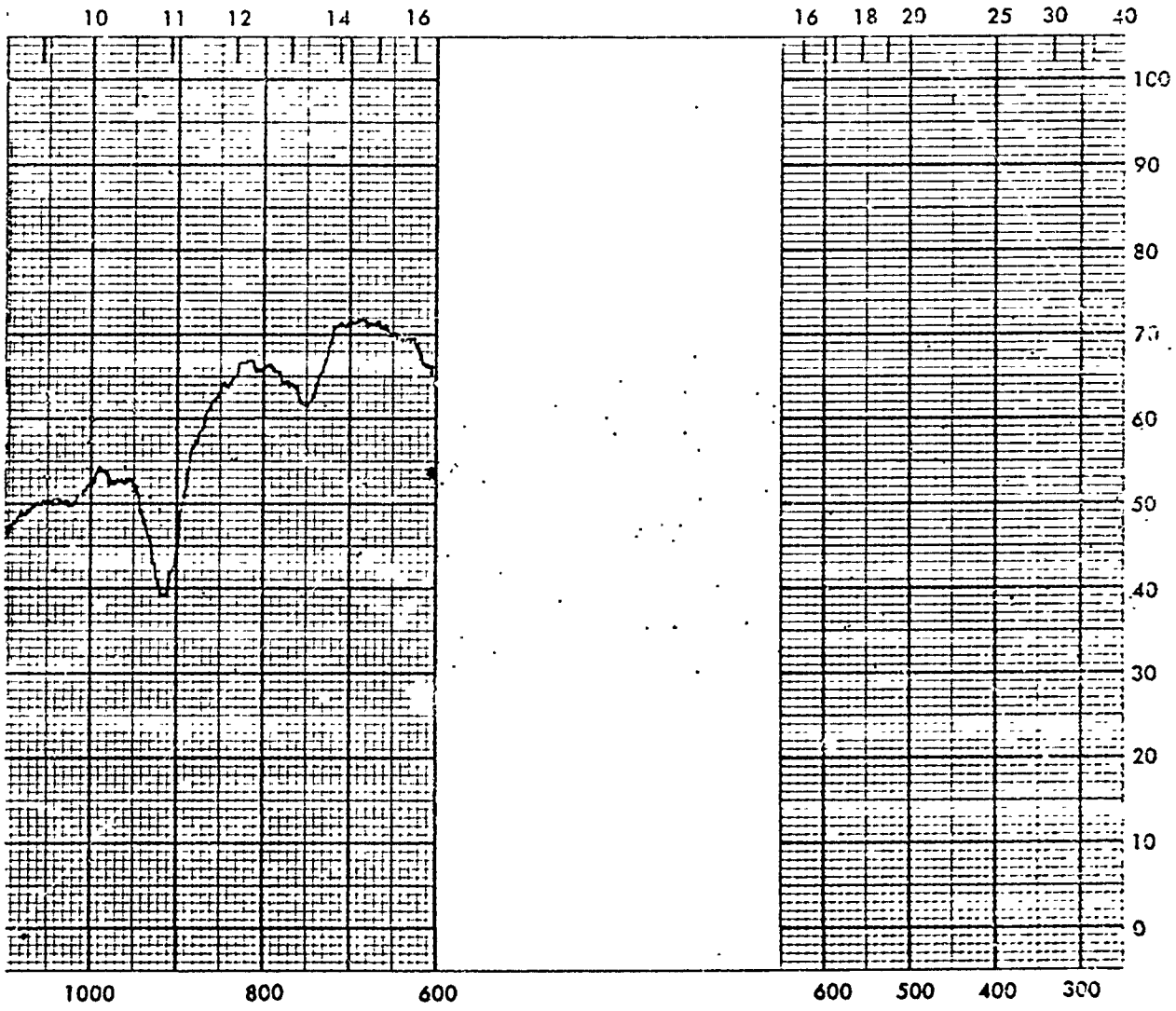


Figure C-12D (Continued). IR Spectrum of RDX Dewater Fraction No. 7



SPECTRUM NO. 4979
DATE 9 Nov 1976
SAMPLE 009-67-8
$CaCl_3$ SOLS
SOURCE BR STIDHAM
STRUCTURE

PATH ____ mm
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS

ANALYST

Beckman
INFRARED
SPECTROPHOTOMETER

Figure C-13D. IR Spectrum of RDX Dewater Fraction No. 8

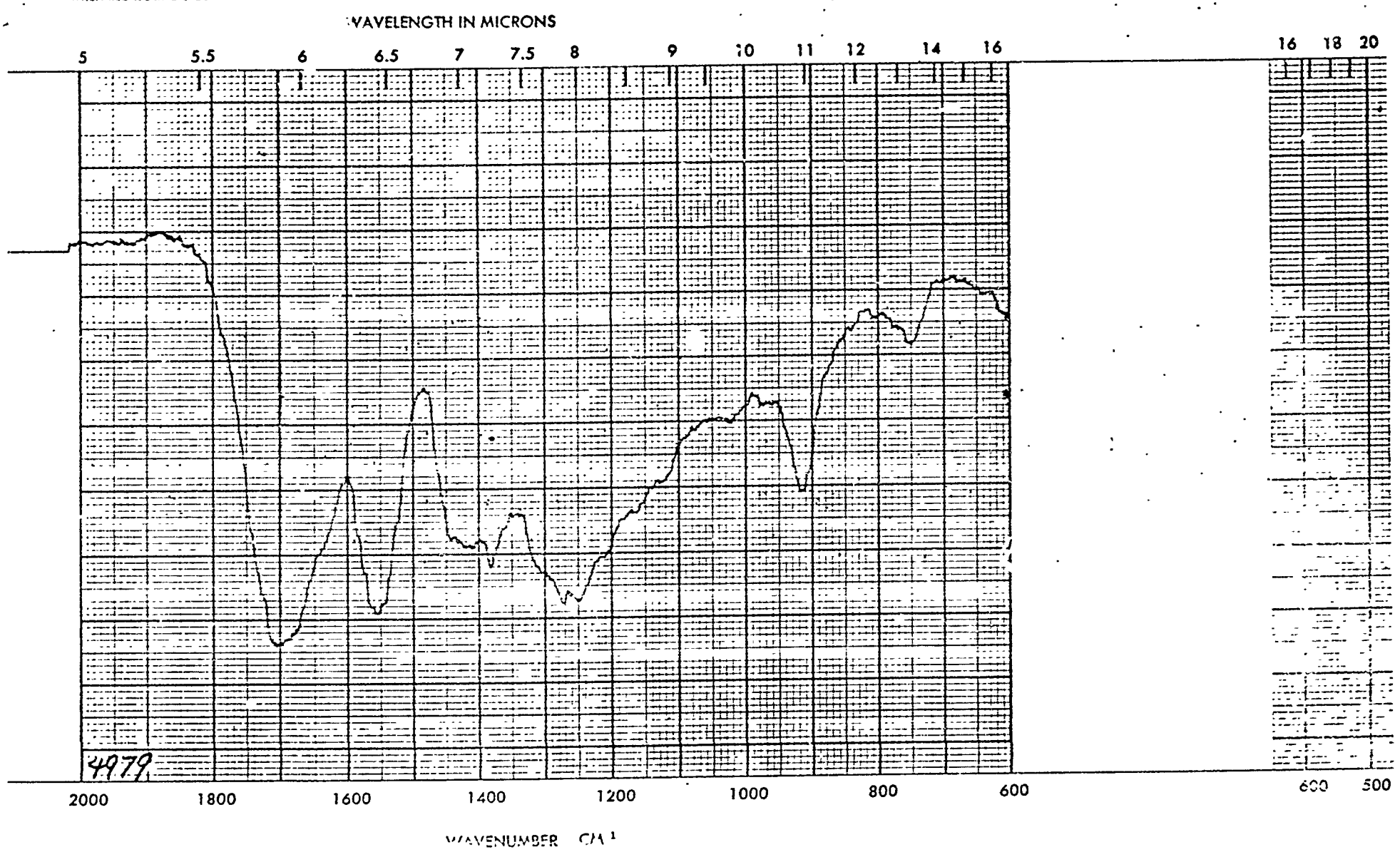


Figure C-13D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

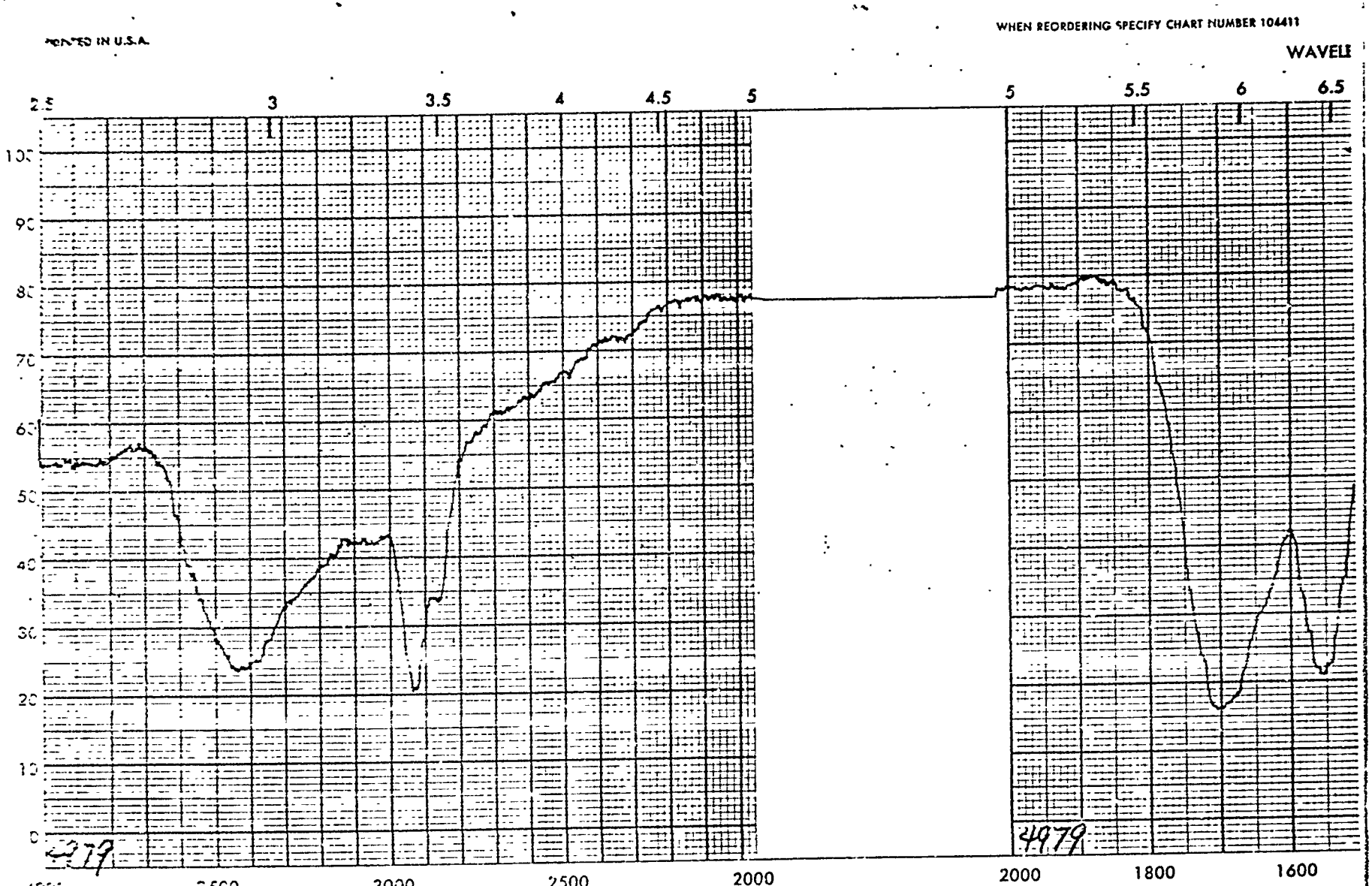


Figure C-13D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

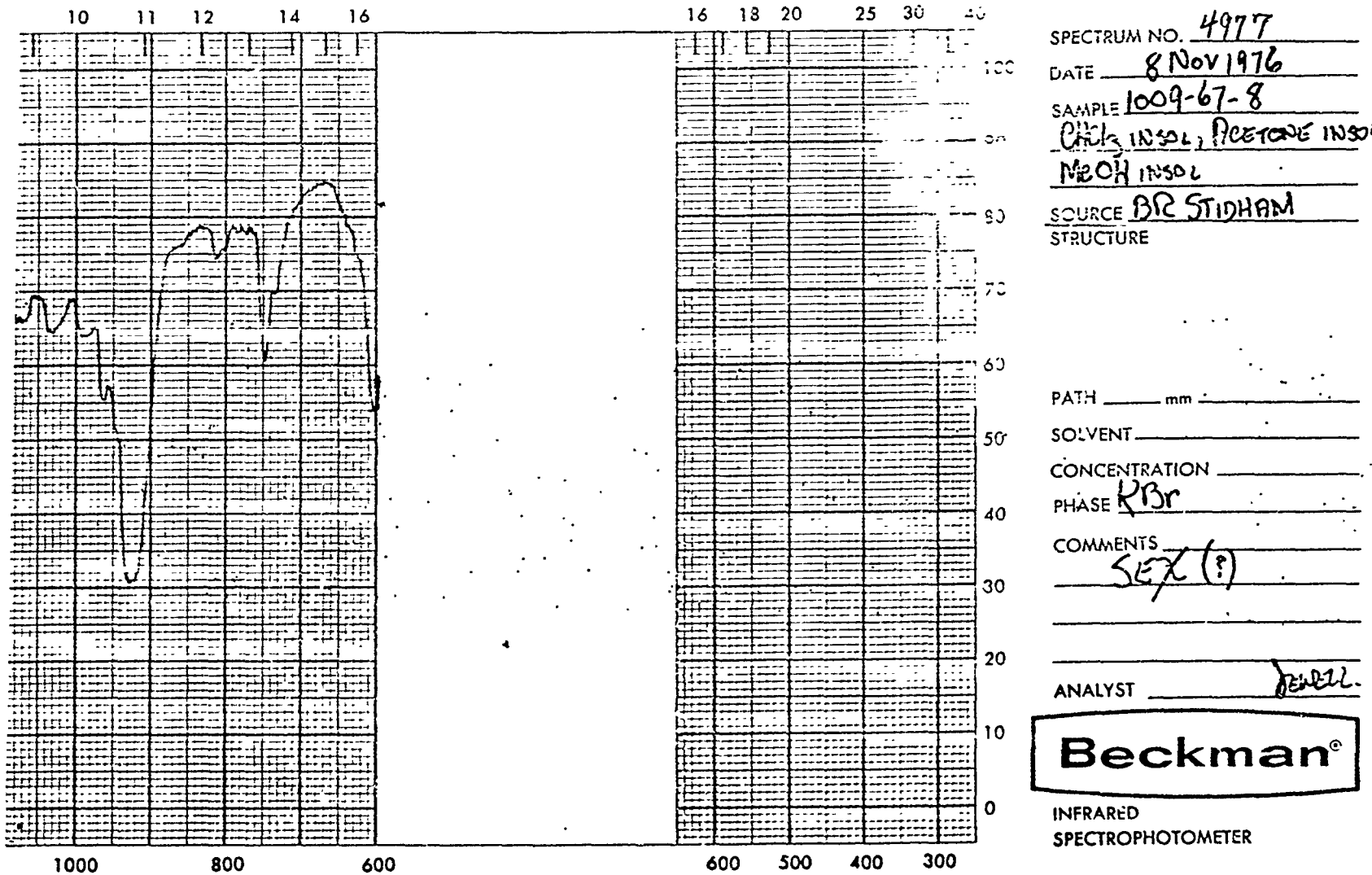


Figure C-14D. IR Spectrum of RDX Dewater Fraction No. 8

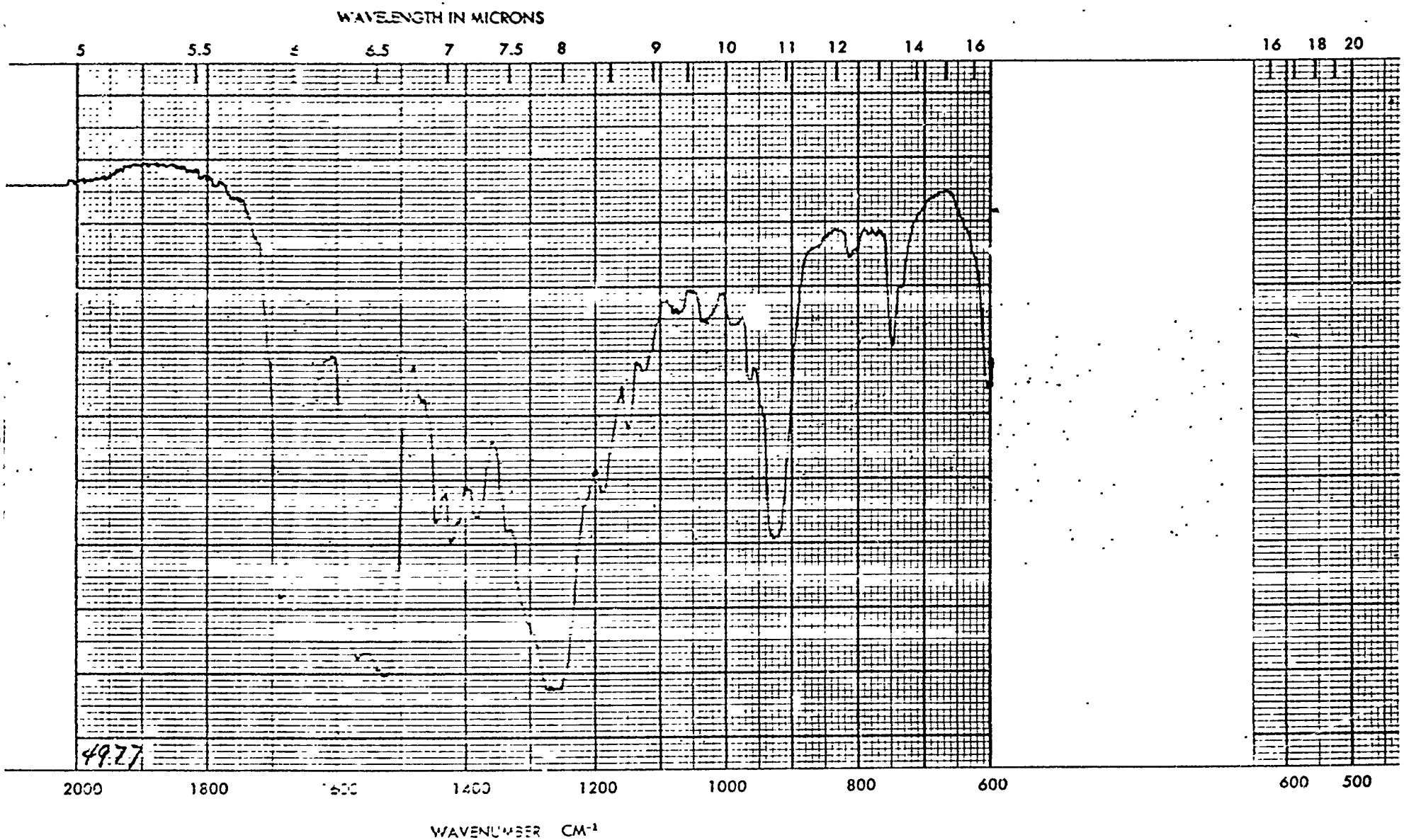


Figure C-14D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

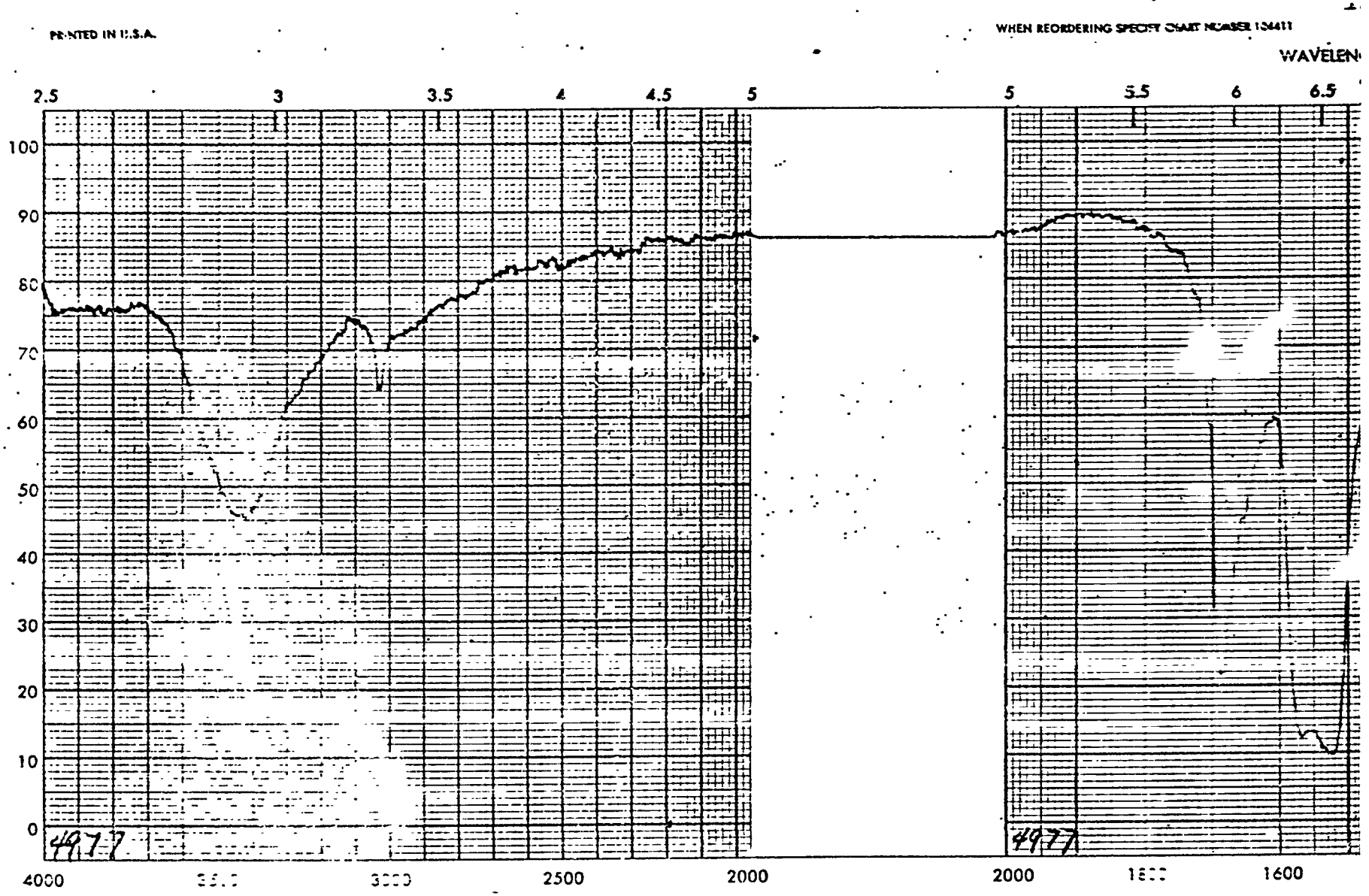
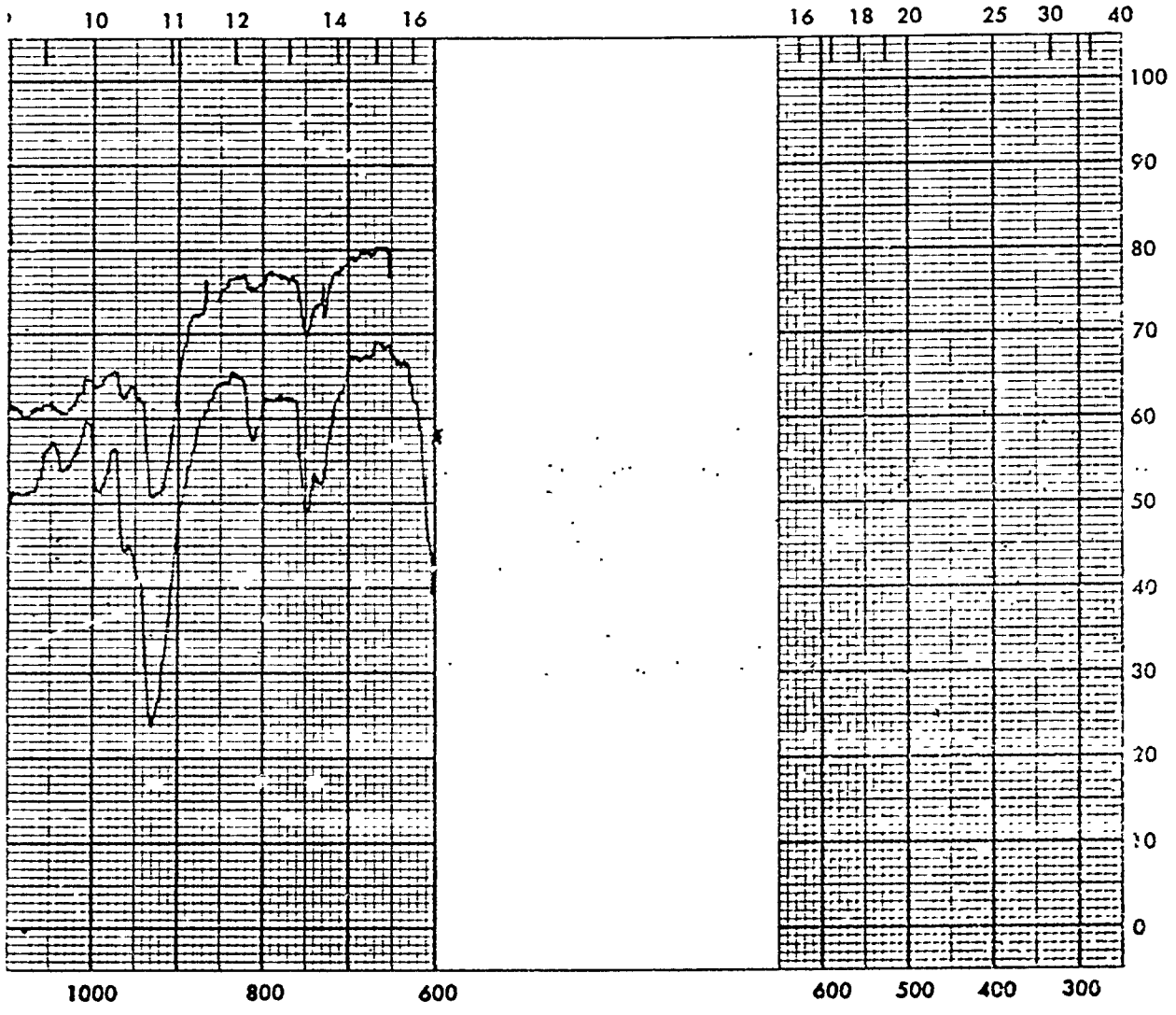


Figure C-14D (Continued). IR Spectrum of RDX Dewater Fraction No. 8



SPECTRUM NO. 4976
DATE 8 NOV 1976
SAMPLE 1009-67-S
$CHCl_3$ INSOL - ACETONE INSOL
SOURCE BRESTIDAM
STRUCTURE
PATH ____ mm
SOLVENT
CONCENTRATION
PHASE KBr
COMMENTS
ANALYST

Beckman®
INFRARED
SPECTROPHOTOMETER

Figure C-15D. IR Spectrum of RDX Dewater Fraction No. 8

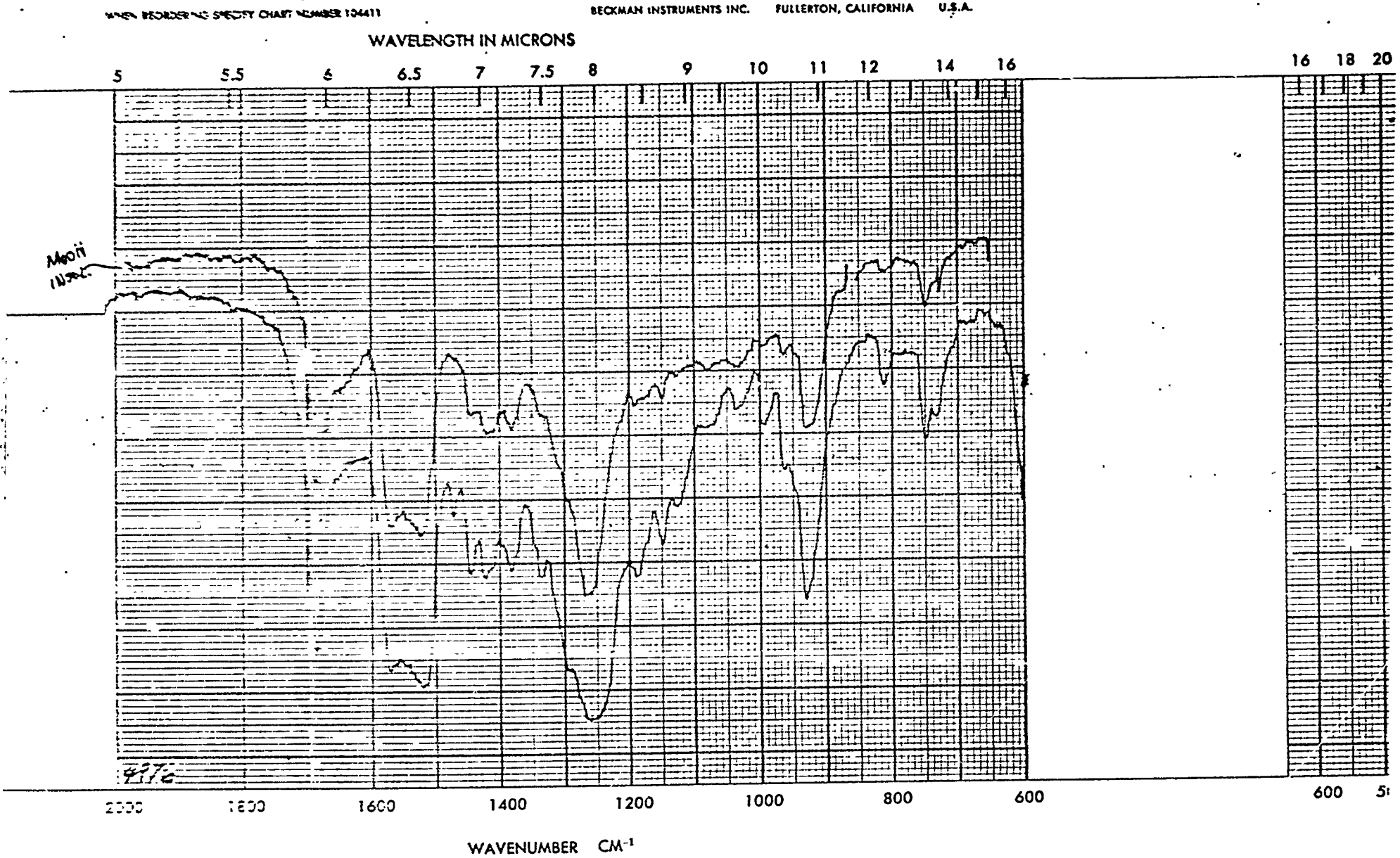


Figure C-15D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

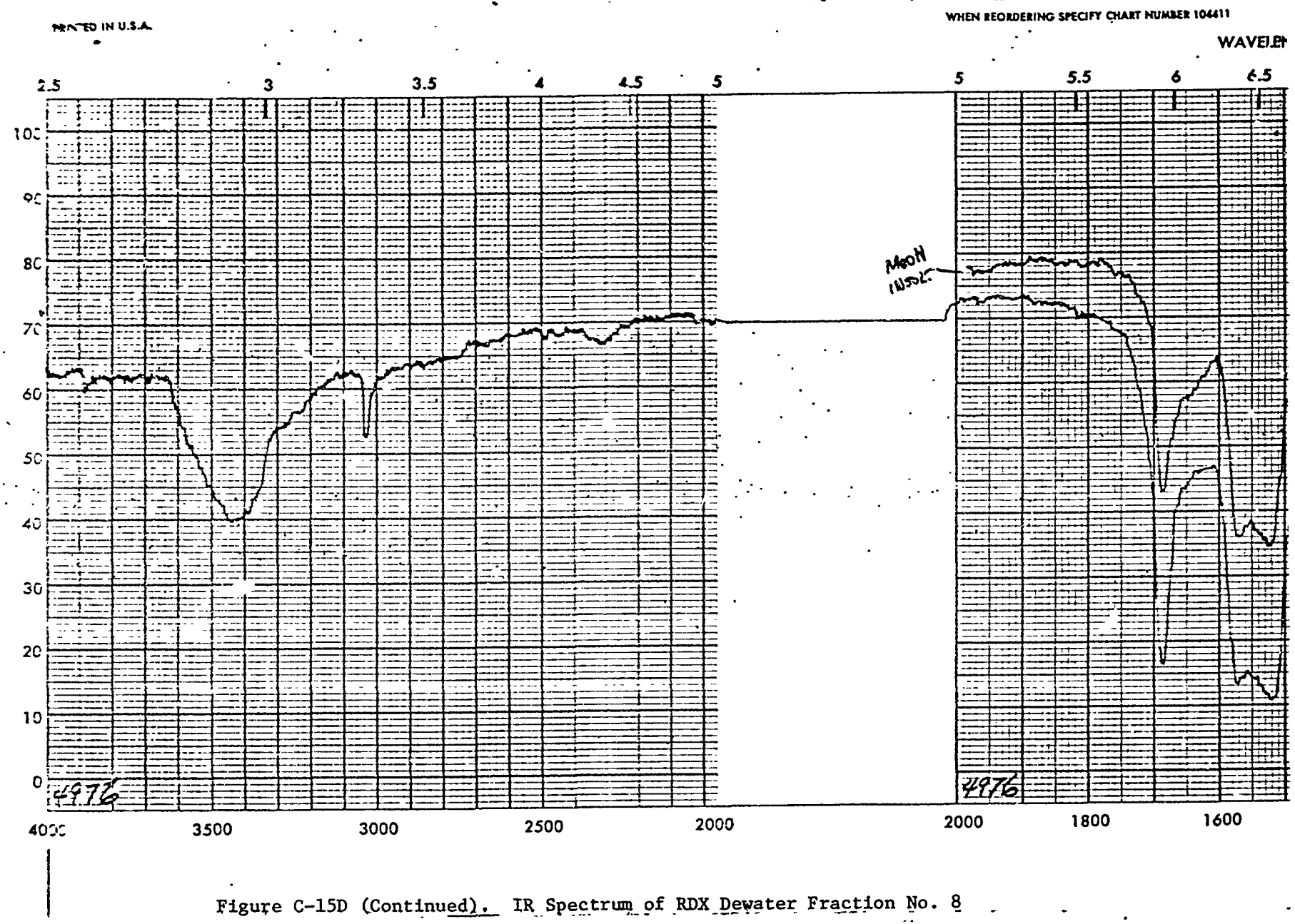


Figure C-15D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

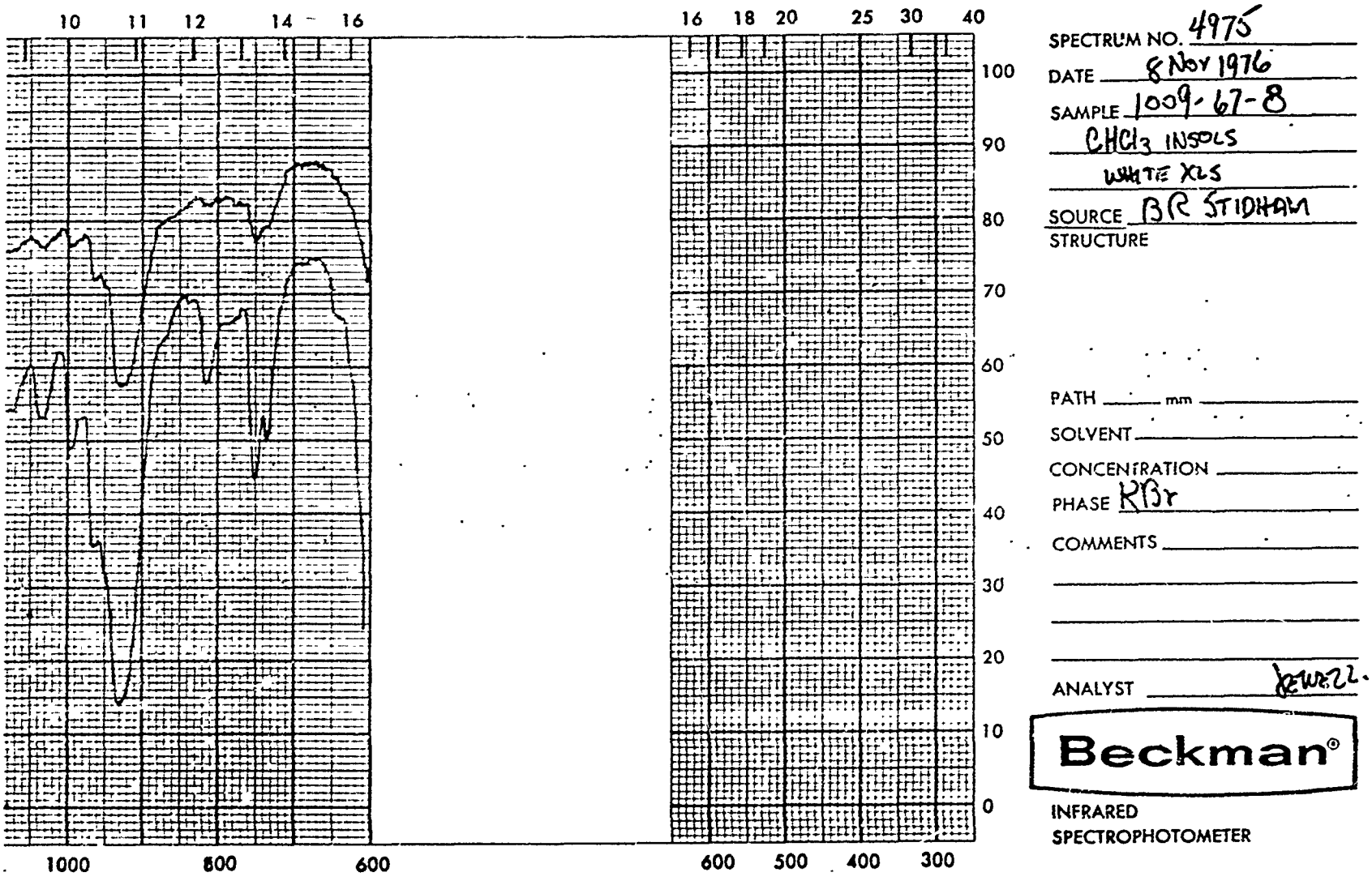


Figure C-16D. IR Spectrum of RDX Dewater Fraction No. 8

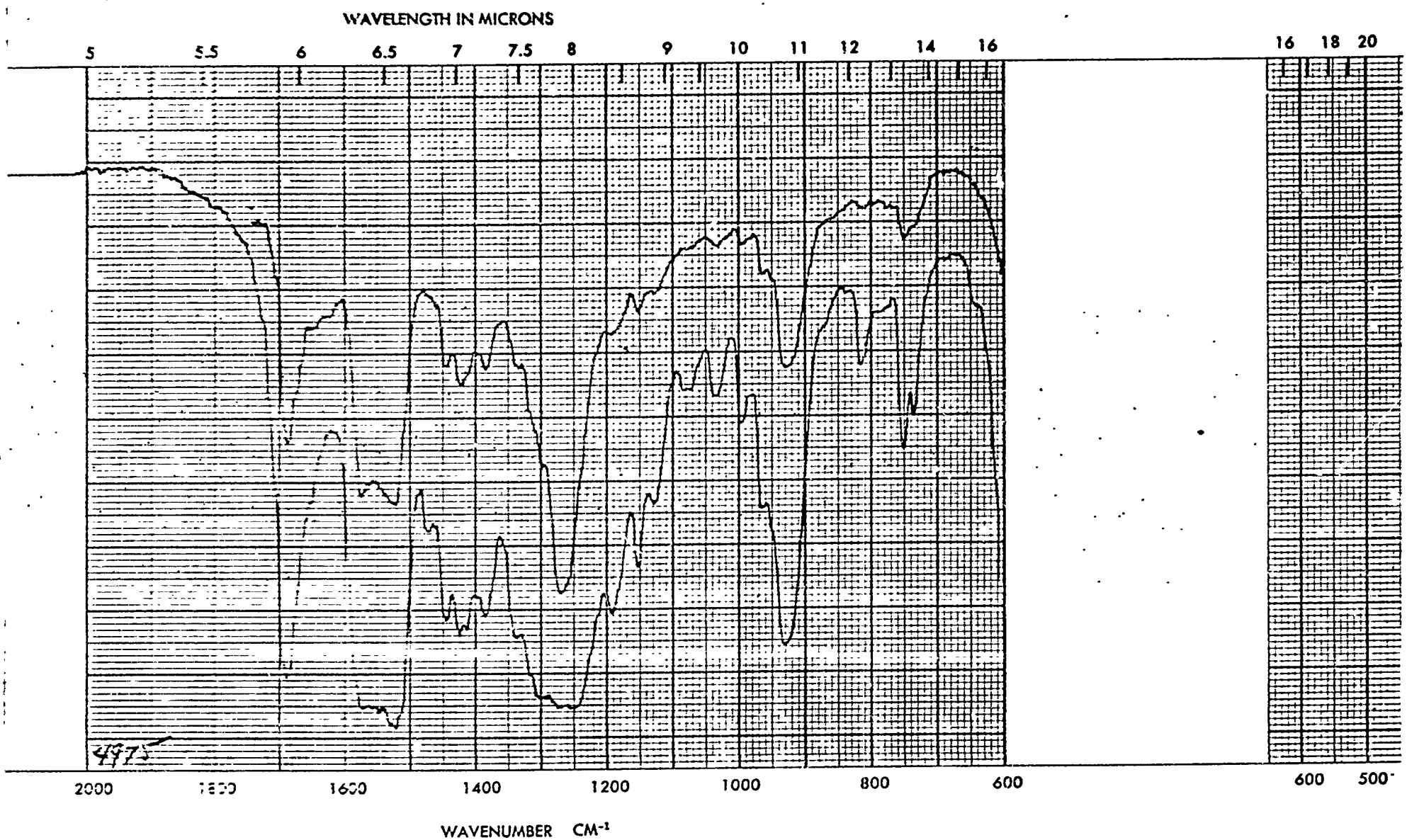


Figure C-16D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

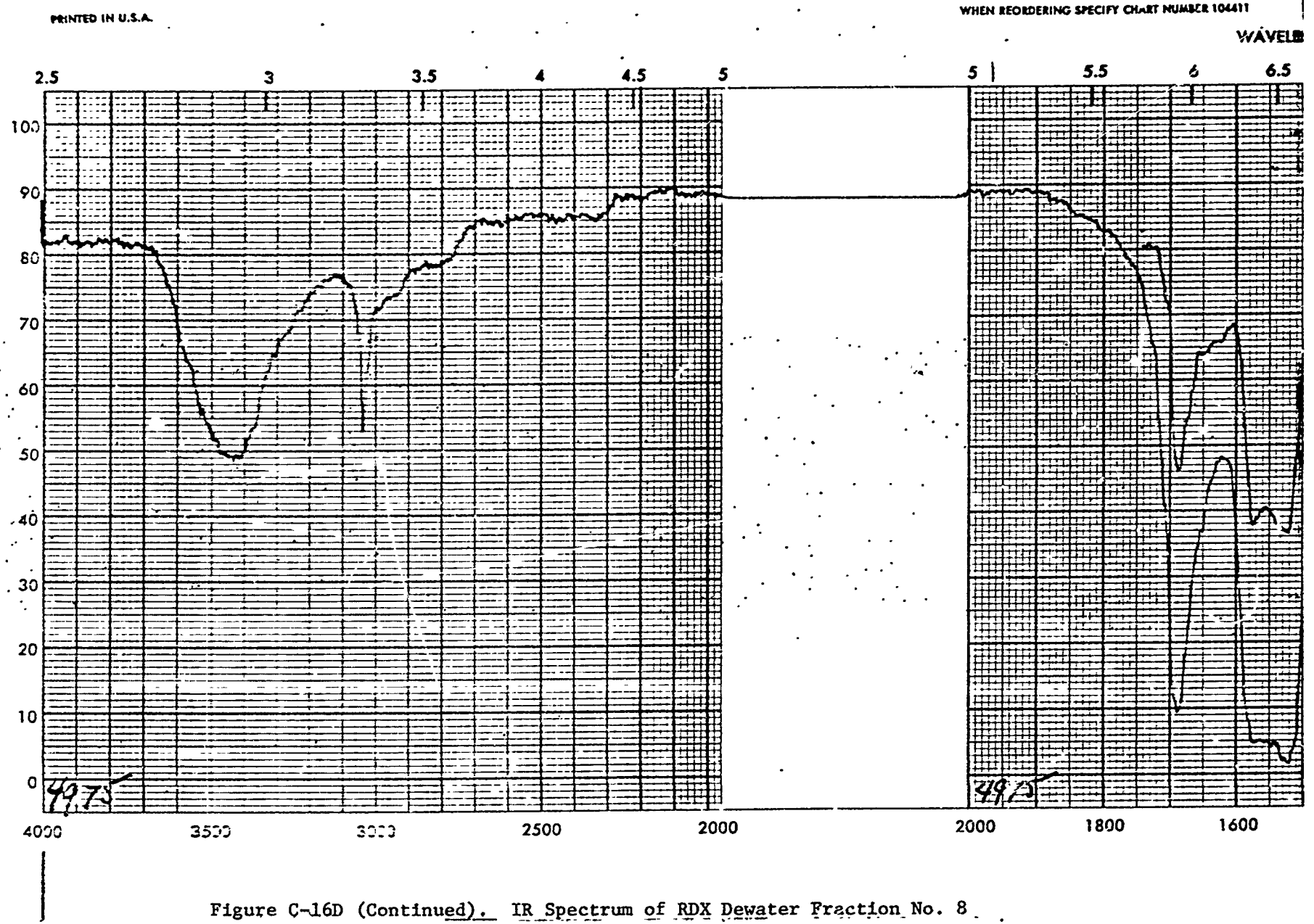


Figure C-16D (Continued). IR Spectrum of RDX Dewater Fraction No. 8

FIGURES C-1E to C-3E

GC CHROMATOGRAMS OF CYCLOHEXANONE DISTILLATES

Pages 160 to 163

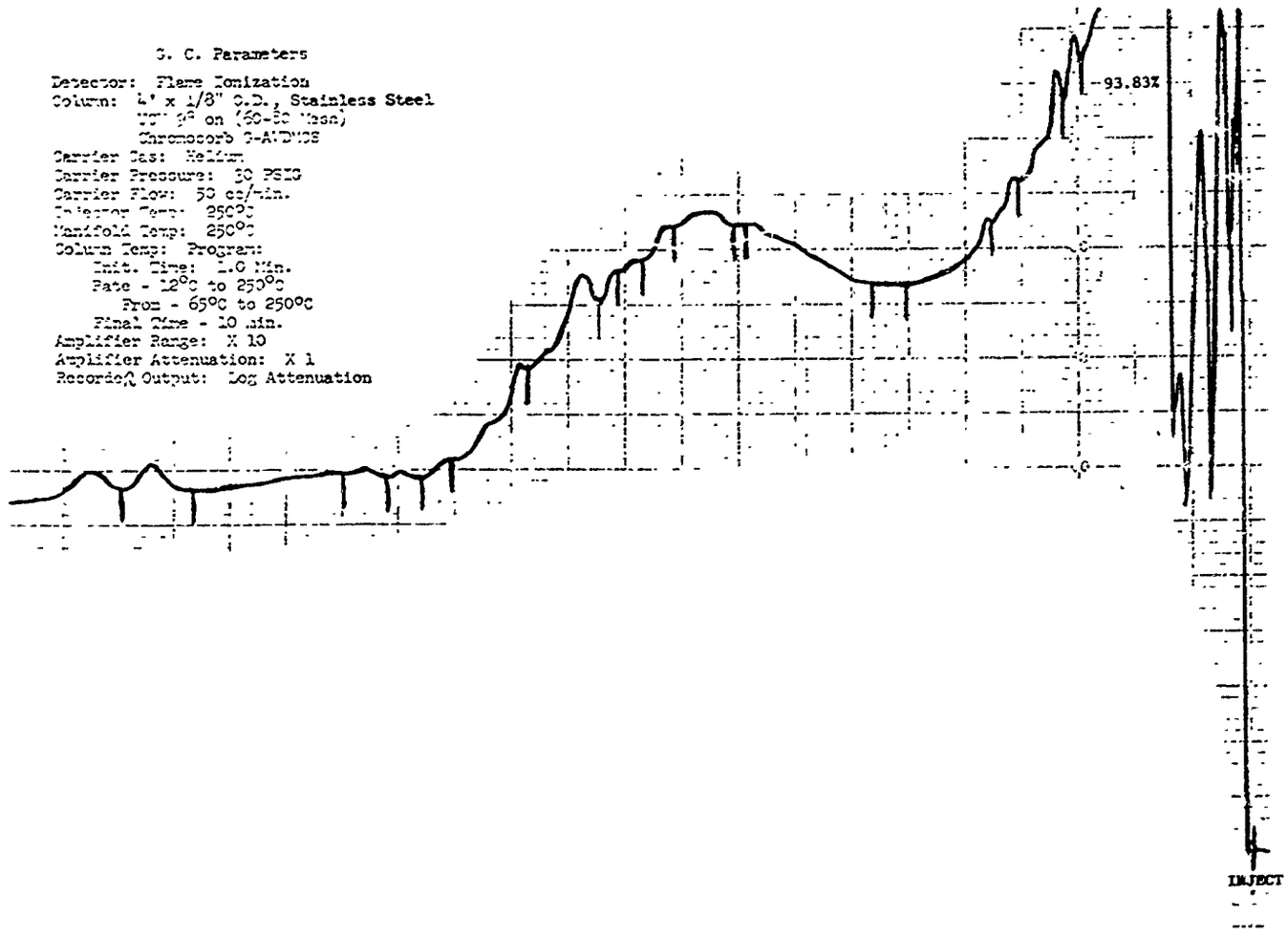


Figure C-1E. GC Chromatogram of Cyclohexanone Distillation-Initial 10%

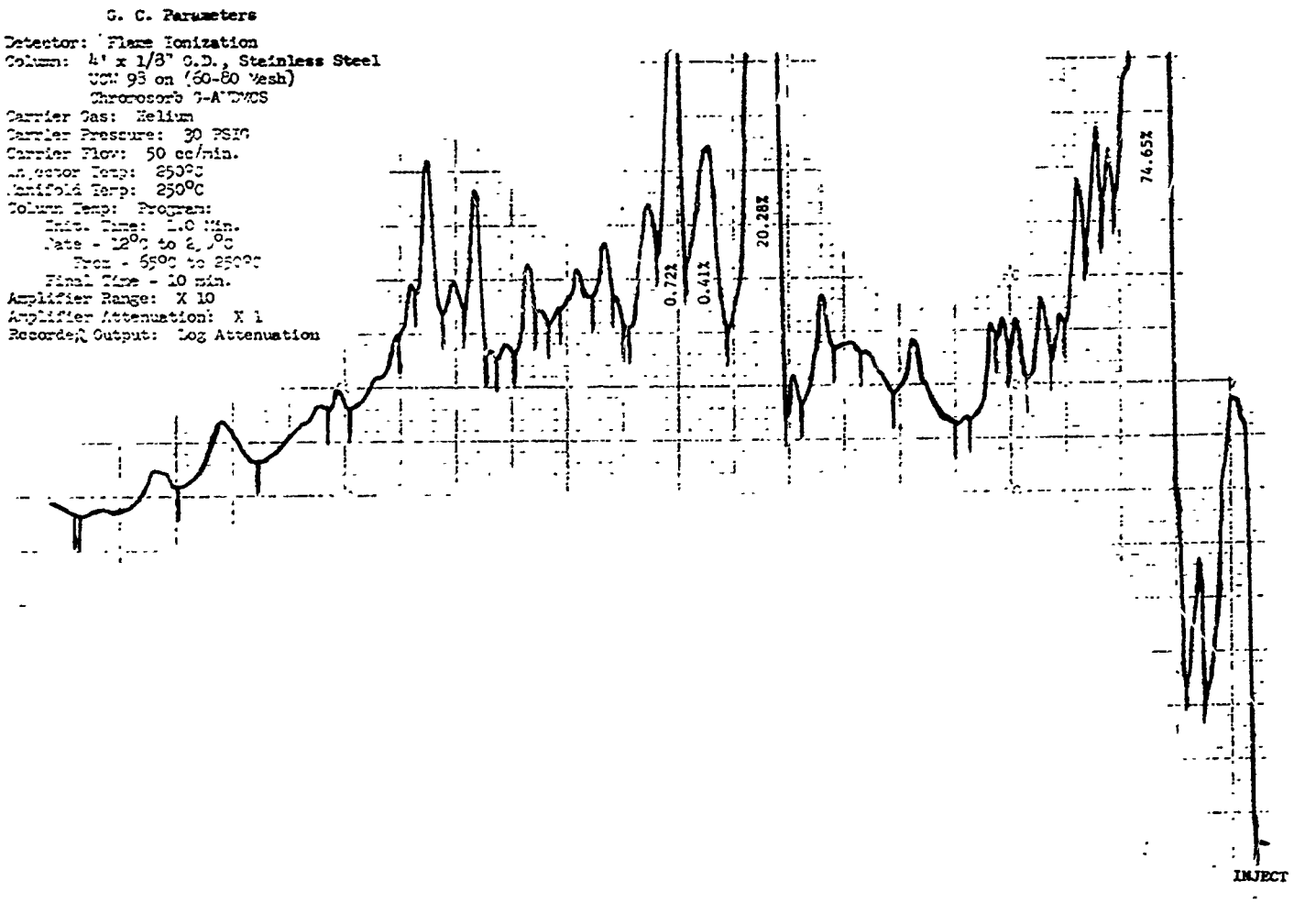


Figure C-2E. GC Chromatogram of Cyclohexanone Distillation - Final 10%

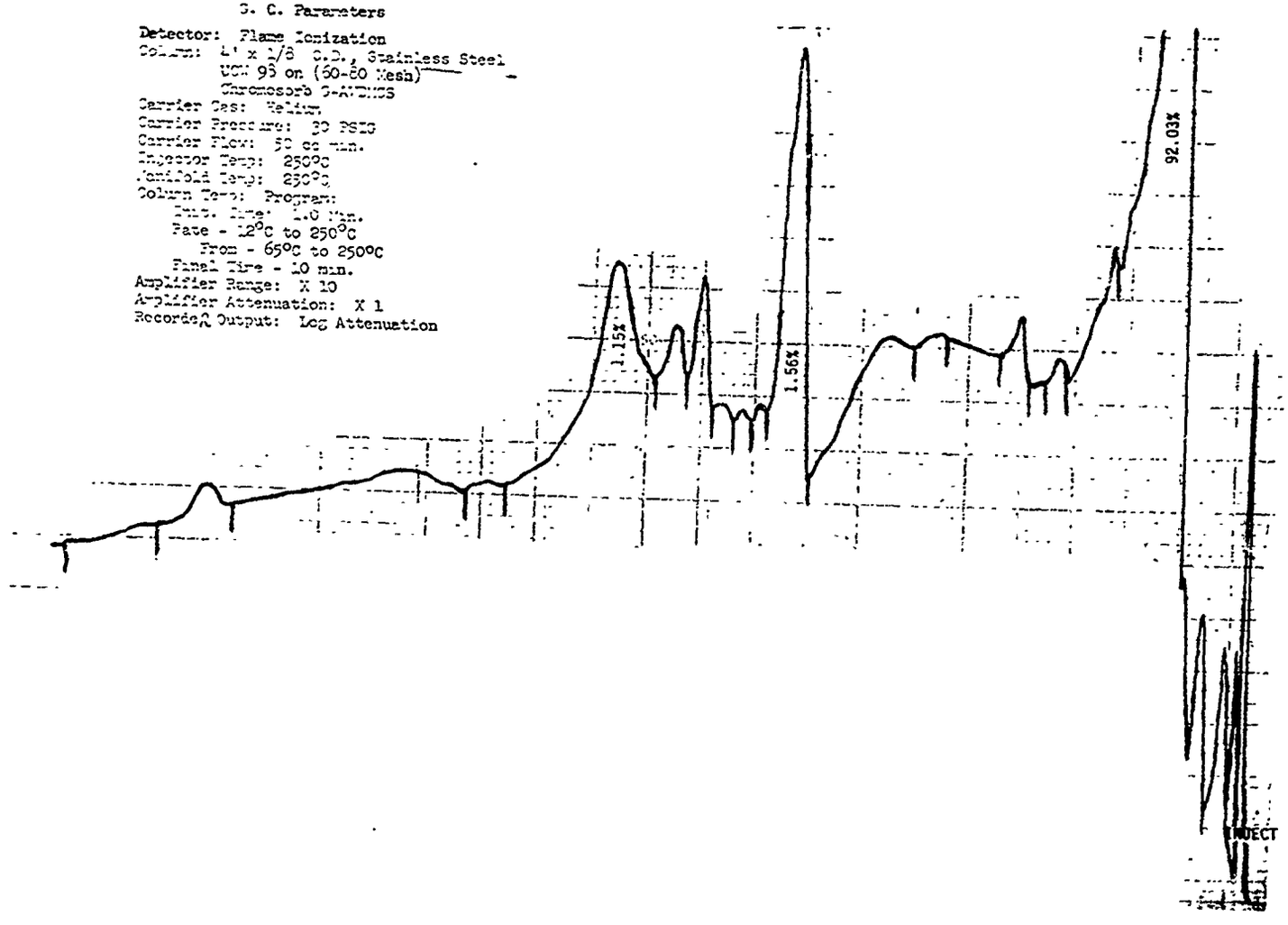


Figure C-3E. GC Chromatogram of Cyclohexanone Distillation - Residue Remaining in Flask After Distillation

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